U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-299 132

Symposium Proceedings: Textile Industry Technology Held at Williamsburg, VA on December 5-8, 1978

Research Triangle Inst, Research Triangle Park, NC

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

May 79

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/2-79-104
May 1979

Research and Development

EPA

Symposium Proceedings: Textile Industry Technology (December 1978, Williamsburg, VA)

PB 299132

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

EPA REVIEW NOTICE

This report has been reviewed by the U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policy of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-79-104	2.	3. RECIPIENT'S ACCESSION NO. PB299132
4. TITLE AND SUBTITLE Symposium Proceedings: Textile Industry Technology (December 1978, Williamsburg, VA)		5. REPORT DATE May 1979
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Frank A. Ayers (Compiler)		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute P.O. Box 12194 Research Triangle Park, North Carolina 27709		10. PROGRAM ELEMENT NO. 1AB604 and 1BB610
		11. CONTRACT/GRANT NO. 68-02-2612, Task 37
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Proceedings; 11/77 - 3/79
		14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Max Samfield, Mail Drop 62, 919/-541-2547.

16. ABSTRACT

The proceedings document most of the approximately 40 presentations at the symposium, December 5-6, 1978, at Williamsburg, VA. The symposium, sponsored by EPA/IERL-RTP's Chemical Processes Branch, provided an exchange of ideas between industry, government, and academic representatives in three related areas: emissions control, energy conservation, and material recovery. There was also a session on assessment methodology. This was the first symposium on textile industry technology sponsored solely by the U.S. EPA. It represents EPA's most extensive technology transfer activity dedicated to support the attainment of pollution control and energy and material conservation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Assessments	Pollution Control	13B
Textile Industry		Stationary Sources	11E
Emission			14B
Conservation			
Energy			
Materials Recovery			07A,13H

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 367
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE A16-A01

EPA Form 2220-1 (9-73)

EPA-600/2-79-104

May 1979

Symposium Proceedings: Textile Industry Technology (December 1978, Williamsburg, VA)

Frank A. Ayers (Compiler)

Research Triangle Institute
P. O. Box 12194
Research Triangle Park, N. C. 27709

Contract No. 68-02-2612
Task No. 37
Program Element Nos. 1AB604 and 1BB610

EPA Project Officer: Max Samfield

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

i. a

ABSTRACT

The proceedings for the "Textile Industry Technology" symposium constitute the final report submitted to the Industrial Environmental Research Laboratory. The symposium was held at Williamsburg, Virginia, December 5-8, 1978.

The purpose of the symposium was to bring about an exchange of ideas in three interrelated areas—emission control, energy conservation, and material recovery. Also a session on assessment methodology was presented. This was the first symposium on textile industry technology sponsored solely by the United States Environmental Protection Agency. This meeting was EPA's most extensive technology transfer activity in the textile area, an activity dedicated to support the attainment of pollution control and energy and material conservation.

CONTENTS

5 December 1978

Page

Keynote Address 1
Stephen J. Gage

Session I: IMPACT OF LEGISLATION ON POLLUTION CONTROL IN THE TEXTILE INDUSTRY
Max Samfield, Session Chairman

Air Pollution Control in the Textile Industry
Donald F. Walters†

Water Pollution Control in the Textile Industry 7
Robert B. Schaffer

RCRA and the Textile Industry 11
Harry W. Trask

The Textile Industry Looks at Pollution Control
Don K. Hill†

Session II: WASTEWATER POLLUTION CONTROL TECHNOLOGY
W. Wesley Eckenfelder, Session Chairman

Origin and Internal Control Options for Priority Pollutants in the Textile Industry 17
Edwin L. Barnhart

Contact Filtration for Textile Wastewater Pollution Control in Poland 23
Jerzy Kurbiel* and
Wieslaw Zymon

Use of Powdered Activated Carbon for Textile Wastewater Pollution Control 37
David G. Hutton* and
Francis L. Robertaccio

Activated Carbon Adsorption for Textile Wastewater Pollution Control 51
E. J. Schroeder* and
A. W. Loven

---

*Indicates speakers
†Indicates papers presented at the conference but not submitted for publication

CONTENTS

Page

Biological Treatment of Textile Waste by Aeration 61
T. A. Alspaugh,
John Hodges, and
Arthur Toompas*

The Use of the Coagulation-Clarification Process in the Treatment of Textile Wastewaters
John H. Koon†

6 December 1978

Session II: WASTEWATER POLLUTION CONTROL TECHNOLOGY (continued)

A Fundamental Approach to Application of Reverse Osmosis for Water Pollution Control 73
S. Sourirajan* and
Takeshi Matsuura

Hyperfiltration of Nonelectrolytes: Dependence of Rejection on Solubility Parameters 107
H. G. Spencer* and
J. L. Gaddis

Separation of Toxic Substances by Hyperfiltration 115
J. Leo Gaddis* and
H. Garth Spencer

Session III: AIR POLLUTION CONTROL TECHNOLOGY
Donald F. Walters, Session Chairman

Incineration and Heat Recovery in the Textile Industry 123
William H. Hebrank

Fixed Bed Carbon Adsorption for Control of Organic Emissions 129
W. Macon Sheppard

Fluidized Bed Activated Carbon Adsorption 141
Ram Chandrasekhar* and
Carmen M. Yon

Catalytic Oxidation of Hydrocarbon Fumes 153
Richard E. Githens* and
Donald M. Sowards

Radiation Curing for Textile Coating 163
William K. Walsh* and
B. S. Gupta

CONTENTS

Page

Control of Airborne Particulates in Textile Plants 171
Mansour H. Mohamed* and
Arthur C. Bullerwell

Session IV: SOLID WASTE POLLUTION CONTROL TECHNOLOGY
P. Aarne Vesilind, Session Chairman

Textile Sludge Characterization 177
Robert G. Shaver* and
Deborah K. Guinan

Dewatering of Waste Activated Sludge 183
Eugene Donovan, Jr.

7 December 1978

Session IV: SOLID WASTE POLLUTION CONTROL TECHNOLOGY (continued)

Characteristics of Activated Sludge Affecting Solid-Liquid Separation
Joseph A. FitzPatrick[†]

Rationale for Sludge Management in a Wastewater Treatment Plant 197
P. Aarne Vesilind

Textile Sludge Treatment and Disposal 201
David H. Bauer,*
John P. Woodyard, and
Stephen P. Shelton

Session V: ASSESSMENT METHODOLOGY
Dale A. Denny, Session Chairman

Level 1 Measurement Procedures for Effluent Characterization 213
R. G. Merrill, Jr.,*
L. D. Johnson, and
J. A. Dorsey

Short-Term Biotesting of Environmental Effluents 225
Shahbeg S. Sandhu

The Testing of Environmental Samples for Mutagenicity and Carcinogenicity Using Microbial Assay Systems 231
Larry D. Claxton,*
Joellen Huisingh, and
Michael Waters

CONTENTS

Page

Cellular Toxicity of Liquid Effluents from Textile Mills 239
James A. Campbell,
Neil E. Garrett,*
Joellen L. Huisingh, and
Michael D. Water

Repeated-Exposure Toxicology Studies 249
Robert J. Weir
(Presented by Ross Hart)

Assessment of Textile Waste Toxicity with Marine Bioassays 251
Gerald E. Walsh* and
Lowell H. Bahner

Freshwater Toxicity Tests Related to the Textile Industry 273
William B. Horning, II* and
Timothy W. Neiheisel

Effluent Guidelines Division Procedures for Measuring Priority Pollutants 281
Roger D. Holm

Organic Sampling and Analysis for Environmental Assessment 297
Philip L. Levins and
Judith C. Harris*

Measurement of Color in Textile Dyeing Wastewaters 307
Linda W. Little

Use of Bioassay Screening Techniques for NPDES Permits 311
W. H. Peltier* and
L. B. Tebo, Jr.

8 December 1978

Session VI: ENERGY AND MATERIALS CONSERVATION
John R. Rossmeissl, Session Chairman

Reclamation of Warp Sizes Using Thermal Precipitation 317
Warren S. Perkins,*
Robert P. Walker, and
Leo J. Hirth

An Industrial Wastewater Recirculation System for the Fibrous Glass Textile Industry 323
S. H. Thomas* and
D. R. Walch

CONTENTS

Page

Optimization of Hyperfiltration System for Renovation of Textile Wastewaters 331
S. M. Ko* and
P. G. Grodzka

Solvent Recovery from Textile Dryers 345
Nathan R. Shaw

Solvent Dyeing of Nylon Carpet Using the STX Solvent Dyeing Process 347
Charles C. Wommack* and
M. Pierre Favier

Reconstitution and Reuse of Dyebaths 363
Wayne C. Tincher,*
Fred L. Cook,
L. Howard Olson, and
W. W. Carr

KEYNOTE ADDRESS

Stephen J. Gage*

When I was sent an advance copy of the program for this symposium, I was pleased for many reasons. First of all, I noted that this is a "multimedia" conference indicating that we in EPA and, hopefully, the textile industry as well, recognize that potential pollution problems exist in the air, in the water, and on land. The interrelationship among these three media must be recognized in solving all pollution problems. For example, one may solve an air pollution problem only to discover that a more severe water pollution problem has been created in the process. Also, we have found instances where toxic materials improperly disposed of in landfills have leached out and polluted local ground waters.

Second, I was pleased to see that government agencies other than EPA's Office of Research and Development are represented: The Department of Energy has a definite role to play, indicating recognition of the need for energy conservation along with requirements for adequate pollution control. Similarly, EPA's Office of Air and Waste Management and the Office of Health and Ecological Effects are represented, recognizing the interdependence of our environmental problems.

Third, I realized in studying the program that government (both Federal and State), the textile industry, universities, and equipment manufacturers are represented in good balance. No one has a monopoly on knowledge, and it is necessary that these four segments of our society share their knowledge and strive toward a common goal: namely, to eliminate whatever pollution problems industry may have and do so in the most efficient and cost-effective manner.

Fourth, I note an entire session is devoted to methodology, with respect both to analytical techniques and to bioassays. We sometimes tend to fall in love with numbers without fully realizing how these numbers were derived and without regard for their accuracy. We must continue to be critical of our methods and refine them to the point where we are confident of the results obtained.

The purpose of setting industrial emissions standards is to protect the health of our people. These standards must, therefore, be the best reflection of what we know about the short-term and long-term health effects of the pollutants. When new data become available, it is essential that this information be transferred to other government agencies, to private scientific groups, and to industries at the earliest possible moment.

The setting of industrial pollution discharge standards is a very complex process involving the legislative and judicial arms of the government, numerous government and private scientific groups, industries, and the public at large. It is thus difficult to clear away the smog of emotions surrounding pollution issues and make decisions on a rational scientific basis. Conferences such as this serve as a sounding board for scientific thought, where industry, universities, and government may exchange ideas and develop new ones. Court cases drain the resources of both industry and the taxpayer. When possible, it is better to resolve problems at the scientific roundtable than to testify in court!

I am well aware of the spirit of cooperation that currently exists between the Environmental Protection Agency and the American Textile Manufacturers' Institute (ATMI), the Northern Textile Association, and the Carpet and Rug Institute. We hope that such cooperation will continue to exist and that out of the mass of data being accumulated will come realistic, cost-effective controls, which both government and industry will consider to be in the best interests of the nation.

I know there is much skepticism on the part of many persons concerning the work of EPA. There have been charges by industry that we are moving too fast and too soon with too little data on which to base decisions. We are further accused of putting industry "out-of-business" because of what is termed excessive pollution control costs.

---

*Assistant Administrator for Research and Development, U.S. EPA, Washington, DC.

The record shows otherwise: The cost of pollution control contributes less than one-half of one percent to the annual rate of inflation (ref. 1). Pollution control creates more jobs as it displaces. Even after adjusting for inflation, corporate profits continue to rise and unemployment is the lowest it has been in several years.

As a result of pressures by EPA to reduce pollution, industry is finding less harmful, substitute materials in many instances. In still other cases, money is actually saved through simultaneous material recovery and energy conservation resulting from efforts to eliminate pollutant discharges to rivers, lakes, and municipal treatment plants. An example of this is the recovery of polyvinyl alcohol sizing agents through the use of ultrafiltration. Judging from your program, many such useful emerging technologies will be discussed during the next 3 days.

The textile industry has been a major contributor to our American standard of living. There are about 7,000 textile plants in the United States, and most of these are on the eastern seaboard. These plants employ almost one million persons and produce products whose gross sales amount to $40 billion annually, representing 0.6 percent of our gross national product on a value-added basis. (ref. 2)

The production of all these goods requires water—lots of water. The textile industry discharges 1 billion gallons of water each day into lakes, streams, and municipal treatment systems. The total value of this water, including the dissolved solids contained in it and the energy in the form of heat, amounts to over $1 million per day. What a golden opportunity to combine pollution control with energy and material recovery!

Industry, however, is not the only segment of our society to cast stones at EPA. Environmental groups, by contrast, accuse EPA of not moving fast enough. They say little has been accomplished. Again, the record shows otherwise: Fish are returning to our lakes and streams. As an example, salmon are returning to the Connecticut River for the first time in years. Fish and other marine life are returning to the Willamette River, the Buffalo River, the Detroit River, and the Houston Ship Channel. (ref. 1)

Similar, though less dramatic, improvements have been made in reducing air pollution: Carbon monoxide levels have fallen, particulate emissions have been reduced, and SO_x levels are measurably smaller. Hopefully, these trends will continue.

The emphasis on pollution control has been changing in recent years, with regulations becoming more and more stringent as additional environmental hazards are recognized. I will not dwell on any of these regulations since I am certain these will be discussed by the overview speakers.

In 1976, a Consent Decree settling a court suit filed under the Federal Water Pollution Control Act was signed by EPA and four environmental groups in which EPA agreed to set effluent standards for 65 classes of compounds for 21 industries, including the textile industry. As a result of the Consent Decree, the Effluent Guidelines Division of EPA published a list of 129 organic pollutants and metals on which they proposed to set regulations. These have become known as the "priority toxic pollutants." Subsequently, amendments to the water pollution legislation, known as the Clean Water Act of 1977, converted the terms of the consent decree into law. Specifically, the 1977 Act requires the application of best available technology economically achievable (BATEA) to control the priority pollutants by July 1, 1984.

These regulations, plus the advent of the Resource Conservation and Recovery Act, the Toxic Substances Control Act, and the forthcoming pretreatment standards of the Clean Water Act, place a great burden on the textile industry. However, we are also aware of the progress the textile industry is making toward solving some of these problems. Most textile plants now have installed biological aeration systems, clarifiers, and finishing ponds, which have enabled the majority of them to meet the 1977 guidelines.

Tertiary treatment systems are being systematically investigated. One such large-scale investigation is, of course, the ATMI/EPA joint project to study the best available technology economically achievable (BATEA), scheduled to be completed this spring. Economic as well as technical studies are being conducted. Some textile plants have already installed advanced water pollution control equipment such as reactor/clarifiers and carbon columns in anticipation of the regulations.

Thus far, my primary emphasis has been on water pollution problems, but I did not intentionally mean to neglect potential air pollution problems. I am pleased that your program intends to cover this aspect. As you well know, the textile industry uses solvents and resins of many types; in dyeing and finishing operations these are volatilized. Once again, ATMI and EPA are cooperating in attempting to determine the nature and extent of these air emissions. Several textile finishing plants have volunteered to have an EPA contractor measure the amount and composition of their emissions. Under other contracts, a state-of-the-art survey for air pollution control technology is being made, which may result in a demonstration grant.

As you are aware, on August 7, 1977, President Carter signed PL 95-95, the Clean Air Act Amendments of 1977. This brings on new responsibilities for the operators of stationary source facilities. This will also change the conditions for obtaining permits for expanded plants and new plants.

Some textile plants have already recognized that they have a serious air pollution problem and have installed incinerator-heat recovery systems or carbon columns. Thus, they also recognize the opportunity for energy and, possibly, material recovery along with air pollution control.

I know that the list of suspected harmful compounds grows larger and larger and that the "pollutant of the month" phase is now uttered jokingly. It is, however, no joking matter, for the incidence of cancer continues to rise significantly. It is, nevertheless, a compliment to our society that we are now balancing our mad rush to produce more and more consumer goods, regardless of long-term consequences, with concern for the long-term health of our population.

Improved epidemiological studies, better analytical techniques, and more sophisticated bioassays are beginning to pinpoint the culprits in our environment, and we are beginning to do something about it. Rules and regulations governing such substances as asbestos, PCB's, PBB's, vinyl chloride, phenols, chromium, and sulfides are only the beginning.

We are fully cognizant, however, of the economic problems facing the textile industry, such as its low profit margin and the threat of foreign imports. It is definitely not EPA's policy to ignore the economic aspects of an industry.

The Toxic Substances Control Act states, in one of its three policy statements, that "authority over chemical substances and mixtures should be exercised in such a manner as not to impede unduly or create unnecessary economic barriers to technological innovation." (ref. 3) This meeting, sponsored by EPA, is testimony to the fact that EPA intends to promote technological innovation when such technology is consistent with our planned policy of pollution control at minimum cost to the industry and to the public.

REFERENCES

1. Remarks by the Honorable Barbara Blum, Deputy Administrator, U.S. EPA, prepared for delivery before the Water Pollution Control Federation, Washington, DC, March 29, 1977.
2. Information obtained from Mr. O'Jay Niles, Director of Technical Services, American Textile Manufacturers' Institute.
3. Quoted from the Toxic Substances Control Act by the Honorable Douglas M. Costle, Administrator, U.S. EPA, at the Center for Continuing Education Seminar on the Federal Regulation of Environmental Carcinogens, the Capital Hilton Hotel, Washington, DC, April 12, 1977.

Session I: IMPACT OF LEGISLATION ON POLLUTION CONTROL IN THE TEXTILE INDUSTRY

Max Samfield, Session Chairman

Preceding page blank

WATER POLLUTION CONTROL IN THE TEXTILE INDUSTRY

Robert B. Schaffer*

Abstract

The textile industry was one of 27 categories of point sources for which effluent limitations and standards were established under the Federal Water Pollution Control Act Amendments of 1972. The first regulations promulgated by the Administrator of EPA affecting the textile industry appeared in the Federal Register *in July 1974. Pretreatment regulations for existing sources in the textile point source category appeared in the* Federal Register *in May 1977. These regulations set forth effluent limitations for existing sources, new source performance standards (NSPS), and pretreatment standards for the textile industry. The pollutant parameters addressed are biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, phenols, sulfides, chromium, color, and pH. And for the wool scouring segment of the industry, oil and grease were also limited.*

The emphasis of the water pollution control program changed on June 7, 1976, when the EPA signed an agreement that settled four lawsuits brought against the Agency by the Natural Resources Defense Council and the Environmental Defense Fund. As a result of this settlement agreement, EPA is charged with the task of developing and promulgating effluent limitations guidelines and standards for 65 toxic substances. This is to be done for 21 major industry categories of which textiles is one.

Table 1 is a list of the 21 major industries set forth in the settlement agreement. Table 2 is a list of the 65 chemical substances for which effluent limitations and guidelines and NSPS and pretreatment standards are to be developed. Since the list of 65 chemical substances is somewhat generic, the Agency was faced with the problem of how to identify specific chemical substances that would meet the requirements for addressing the 65 substances listed in the settlement agreement. Table 3 is a list of 129 specific chemical substances (114 organics, 13 heavy metals, cyanide, and asbestos) representative of the 65 generic substances set forth in the settlement agreement.

The 1977 Amendments to the Clean Water Act recognized the significance of the settlement agreement and emphasized the importance of the Agency's toxics control strategy. The new Act directed EPA to concentrate on the pollution problems causing the most concern and to reevaluate the areas where progress had already been made. Of the 129 chemicals mentioned earlier, 29 have been determined to be most significant in textile effluents (see Table 4). Others have been suggested as possible constituents of textile mill wastes by industry sources but have not been detected in the field sampling program and are not presently considered as important as the 29 chemicals in Table 4. The control of these substances will be the subject of the best available technology (BAT), NSPS, and pretreatment regulations for toxic pollutants.

The progress in controlling nontoxic discharges through the earlier effluent limitations was reflected in Section 304 (b)(4) of the Act which mandated that conventional pollutants such as BOD, COD, suspended solids, and pH be controlled under best conventional pollutant control technology (BCT). This replaced BAT for control of conventional pollutants. If it is determined that effluents from some textile subcategories contain only conventional pollutants, EPA would issue BCT regulations for those subcategories when the BAT guidelines for toxics are issued. Congress specified that BCT could be equal to or more stringent than best practicable treatment (BPT). BCT will be determined for each industrial subcategory after balancing the costs with the effluent reduction benefits. BCT permits would not be eligible for economic variances or water quality variances.

Not all pollutants are classified as conventional or toxic pollutants under the Act. Pollut-

---

*Director, Effluent Guidelines Division, U.S. Environmental Protection Agency, Washington, DC.

Preceding page blank

TABLE 1. INDUSTRIES COVERED BY CONSENT DECREE

Timber products processing
Leather tanning and finishing
Steam electric power plants
Iron and steel manufacturing
Petroleum refining
Nonferrous metals manufacturing
Paint and ink formulation and printing
Auto and other laundries
Paving and roofing materials
Ore mining and dressing
Coal mining
Textile mills
Soap and detergent manufacturing
Plastic and synthetic materials manufacturing
Pulp and paperboard mills; converted paper products
Rubber processing
Miscellaneous chemicals
Machinery and mechanical products manufacturing
Electroplating
Inorganic chemicals manufacturing
Organic chemicals manufacturing

TABLE 2. SETTLEMENT AGREEMENT POLLUTANTS

Acenaphthene
Acrolein
Acrylonitrile
Aldrin/dieldrin
Antimony and compounds
Arsenic and compounds
Asbestos
Benzene
Benzidine
Beryllium and compounds
Cadmium and compounds
Carbon tetrachloride
Chlordane
Chlorinated benzenes
Chlorinated ethanes
Chloroalkyl ethers
Chlorinated naphthalene
Chlorinated phenols
Chloroform
2-chlorophenol
Chromium and compounds
Copper and compounds
Cyanides
DDT and metabolites
Dichlorobenzene
Dichlorobenzidine
Dichloroethylenes
2,4-dichlorophenol
Dichloropropane and dichloropropene
2,4-dimethylphenol
Dinitrotoluene
Diphenylhydrazine
Endosulfan and metabolites
Endrin
Ethylbenzene
Fluoranthene
Haloethers
Halomethanes
Heptachlor and metabolites
Hexachlorobutadiene
Hexachlorocyclohexane
Hexachlorocyclopentadiene
Isophorone
Lead and compounds
Mercury and compounds
Naphthalene
Nickel and compounds
Nitrobenzene
Nitrophenols
Nitrosamines
Pentachlorophenol
Phenol
Phthalate esters
Polychlorinated biphenyls
Polynuclear aromatic hydrocarbons
Selenium and compounds
Silver and compounds
2,3,7,8-tetrachlorodibenzo-p-dioxin
Tetrachloroethylene
Thallium and compounds
Toluene
Toxaphene
Trichloroethylene
Vinyl chloride
Zinc and compounds

TABLE 3. SPECIFIC CHEMICAL SUBSTANCES TO BE EXAMINED

1. Acenaphthene*
2. Acrolein*
3. Acrylonitrile*
4. Benzene*
5. Benzidine*
6. Carbon tetrachloride*

Chlorinated benzenes*

7. Chlorobenzene
8. 1,2,4-trichlorobenzene
9. Hexachlorobenzene

Chlorinated ethanes*

10. 1,2-dichloroethane
11. 1,1,1-trichloroethane
12. Hexachloroethane
13. 1,1-dichloroethane
14. 1,1,2-trichloroethane
15. 1,1,2,2-tetrachloroethane
16. Chloroethane

Chloroalkyl ethers*

17. bis(chloromethyl) ether
18. bis(2-chloroethyl) ether
19. 2-chloroethyl vinyl ether

Chlorinated napthalene*

20. 2-chloronaphthalene

Chlorinated phenols*

21. 2,4,6-trichlorophenol
22. Panachlorometa cresol
23. Chloroform*
24. 2-chlorophenol*

Dichlorobenzenes*

25. 1,2-dichlorobenzene
26. 1,3-dichlorobenzene
27. 1,4-dichlorobenzene

Dichlorobenzidine*

28. 3,3-dichlorobenzidine

Dichloroethylenes*

29. 1,1-dichloroethylene
30. 1,2-trans-dichloroethylene
31. 2,4-dichlorophenol*

Dichloropropane and dichloropropene*

32. 1,2-dichloropropane
33. 1,3-dichloropropylene
34. 2,4-dimethylphenol*

Dinitrotoluene*

35. 2,4-dinitrotoluene
36. 2,6-dinitrotoluene
37. 1,2-diphenylhydrazine*
38. Ethylbenzene*
39. Fluroanthene*

Haloethers*

40. 4-chlorophenyl phenyl ether
41. 4-bromophenyl phenyl ether
42. bis(2-chloroisopropyl) ether
43. bis(2-chloroethoxy) methane

Halomethanes*

44. Methylene chloride
45. Methyl chloride
46. Methyl bromide
47. Bromoform (tribromomethane)
48. Dichlorobromomethane
49. Trichloroflouromethane
50. Dichlorodifluoromethane
51. Chlorodibromomethane
52. Hexachlorobutadiene*
53. Hexachlorocyclopentadiene*
54. Isophorone*
55. Naphthalene*
56. Nitrobenzene*

Nitrophenols*

57. 2-nitrophenol
58. 4-nitrophenol
59. 2,4-dinitrophenol*
60. 4,6-dinitro-o-cresol

Nitrosamines*

61. N-nitrosodimethylamine
62. N-nitrosodiphenylamine
63. N-nitrosodi-n-propylamine
64. Pentachlorophenol*
65. Phenol*

Pthlate esters

66. bis(2-ethylhexyl) phthalate
67. Butyl benzyl phthalate
68. di-n-butyl phthalate
69. di-n-octyl phthalate
70. Diethyl phthalate
71. Dimethyl phthalate

Polynuclear aromatic hydrocarbons*

72. 1,2-benzanthracene
73. Benzo(a)pyrene (3,4-benzopyrene)
74. 3,4-benzofluoranthene
75. 11,12-benzofluoranthene
76. Chrysene
77. Acenaphthylene
78. Anthracene
79. 1,12-benzoperylene
80. Fluorene
81. Phenanthrene
82. 1,2,5,6-dibenzanthracene
83. Indenol(1,2,3-cd)pyrene
84. Pyrene
85. Tetrachloroethylene*
86. Toluene*
87. Tryichloroethylene*
88. Vinyl chloride (chloroethylene)*

Pesticides and metabolites

89. Aldrin*
90. Dieldrin*
91. Chlordane*

DDT and metabolites

92. 4,4'-DDT
93. 4,4'-DDE (p,p'-DDX)
94. 4,4'-DDD (p,p'-TDE)

Endosulfan and metabolites*

95. a-ensodulfan-alpha
96. b-endosulfan-beta
97. Endosulfan sulfate

Endrin and metabolites*

98. Endrin
99. Endrin aldehyde

Heptachlor and metabolites*

100. Heptachlor
101. Heptachlor epoxide

Hexachlorocyclohexane*

102. a-BHC-alpha
103. b-BHC-beta
104. r-BHC (lindane)-gamma
105. g-BHC-delta

Polychlorinated biphenyls (PCB's)*

106. PCB-1242 (Arochlor 1242)
107. PCB-1254 (Arochlor 1254)
108. PCB-1221 (Arochlor 1221)
109. PCB-1232 (Arochlor 1232)
110. PCB-1248 (Arochlor 1248)
111. PCB-1260 (Arochlor 1260)
112. PCB-1016 (Arochlor 1016)
113. Toxaphene*
114. Antimony (total)*
115. Arsenic (total)*
116. Asbestos (fibrow)*
117. Beryllium (total)*
118. Cadmium (total)*
119. Chromium (total)*
120. Copper (total)*
121.Cyanide (total)*
122. Lead (total)*
123. Mercury (total)*
124. Nickel (total)*
125. Selenium (total)*
126. Silver (total)*
127. Thallium (total)*
128. Zinc (total)*
129. 2,2,7,8-tetrachlorodibenzo-p-dioxin (TCDD)*

---

*Specific compounds and chemical classes as listed in the consent decree

Note: Ambiguous compounds or classes of compounds are underlined.

TABLE 4. MOST SIGNIFICANT TOXIC POLLUTANTS IN TEXTILE WASTEWATERS

Acrylonitrile
Benzene
1,2,4-trichlorobenzene
2,4,6-trichlorophenol
Parachlorometacresol
Chloroform
1,2-dichlorobenzene
Ethylbenzene
Trichlorofluoromethane
Naphthalene
N-nitrosodi-n-propylamine
Pentachlorophenol
Phenol
bis(2-ethylhexyl) phthalate
Tetrachloroethylene
Toluene
Trichloroethylene
Antimony
Arsenic
Cadmium
Chromium
Copper
Cyanide
Lead
Mercury
Nickel
Selenium
Silver
Zinc

ants such as color do not fall into either category and are called nonconventional pollutants. If it is determined that effluents from textile subcategories require color removal, EPA would issue BAT regulations for this nonconventional pollutant when the BAT guidelines for toxics are issued. Unlike regulations covering conventional or toxic pollutants, economic variances and water quality variances can be granted.

It is clear that the effluent regulations presently under consideration for the textile industry include toxic, conventional, and nonconventional pollutants. While the effort has become known as the BAT Revision Program, the regulations include NSPS and pretreatment standards in addition to effluent guidelines for dischargers to receiving waters. The development and implementation of pretreatment standards for mills discharging into publicly owned treatment works (POTW) is the subject of a separate paper. However, a few comments may be helpful.

The general pretreatment regulations were promulgated on June 26, 1978. The major components of the Agency's pretreatment strategy include: (1) technology based pretreatment standards for toxic pollutants, (2) strong encouragement, including financial incentives for local enforcement of pretreatment standards, and (3) modifications of the standards for POTW with documented pollutants removal efficiencies. The pretreatment standards will be developed by applying BAT decision criteria to indirect dischargers in accordance with the Agency's pretreatment strategy with an aim toward limiting the impact of textile dischargers on POTW's and receiving waters while avoiding to the extent possible redundant treatment by industry and municipalities.

The settlement agreement set forth a schedule for the textile industry program to complete the technical and economic studies and to propose and promulgate regulations. The technical report that contains the findings of our contractor, Sverdrup & Parcel, St. Louis, Missouri, has been circulated to other Federal offices, States, industry, and other public interest groups for review and comment. The draft economic analysis has also been completed by Development Planning and Research Associates, Inc., Manhattan, Kansas. Soon the technologies available for control and treatment of various pollutants will be evaluated with the cost and economic impacts of the various options and with the toxicity and exposure levels of the various pollutants. This integration of technical, economic, and environmental considerations will culminate in a proposed regulation for the textile industry in May 1979, with final promulgation expected in December. As we proceed to develop these standards, we plan to continue to invite active participation—public, industrial, community, as well as environmental groups—and we will continue to solicit industrial input and assistance.

RCRA AND THE TEXTILE INDUSTRY

Harry W. Trask*

Abstract

Congress passed the Resource Conservation and Recovery Act (RCRA) in October 1976. The stated objectives of RCRA are to promote the protection of health and the environment and to conserve valuable material and energy resources. The Act intends that these objectives be achieved by: providing technical and financial assistance to State and local governments for development and implementation of solid waste management plans; prohibiting future open dumping on land and requiring upgrading or closing of existing open dumps; regulating the treatment, storage, transportation, and disposal of hazardous waste; promulgating guidelines for solid waste management practices and systems; conducting a research and development program for improved solid waste management and resource conservation techniques; demonstrating improved solid waste management and resource conservation and recovery systems; and establishing a cooperative effort among Federal, State, and local governments and private enterprises.

The Act statutorily establishes the Office of Solid Waste within EPA to guide the implementation of the law and establishes a Federal/State/local government partnership to share the implementation. The major thrusts of the efforts that will be required by this partnership are: land protection through regulation and control of wastes and waste disposal operations; regulations to control the hazardous waste stream from "cradle to grave;" reduction of the waste stream through increased resource recovery and waste reduction efforts; public education programs with rapid dissemination of all types of solid and hazardous waste management information materials; and extensive public participation in the development and improvement of solid waste management throughout the Nation.

The regulatory part of the Act, the part dealing with control of hazardous wastes, will be the subject of the remainder of this paper. But first, consideration will be given to the overall problem of hazardous wastes.

THE HAZARDOUS WASTE PROBLEM

According to the results of 17 recent EPA industry studies, an estimated 34 million metric tons (wet basis) of potentially hazardous industrial waste were generated in 1977. The amount generated is expected to increase with industry growth and more pollution control. Approximately 80 percent of this waste is managed onsite by the generators, the remaining 20 percent being hauled offsite for disposal by contractors.

In the textile industry, certain wastewater treatment sludges may be hazardous wastes depending on their constituents. For example, sludges from wool scouring and certain fabric dyeing and finishing operations may contain toxics such as lead, chromium, arsenic, cadmium, mercury, etc. It is estimated that about 1.7 million metric tons (wet weight) of hazardous or potentially hazardous wastes were generated by the textile industry in 1977.

The method most used for disposal of hazardous industrial waste is lagooning in unlined surface impoundments, accounting for nearly half of the total. The second most common practice is dumping in nonsecure landfills. Together these receive almost 80 percent of all hazardous wastes. An additional 10 percent is accounted for by uncontrolled incineration. Thus, 90 percent of the potentially hazardous wastes generated by the 17 key industries are managed by practices inadequate for protection of human health and the environment.

The consequences of illegal or inadequate disposal can be quite harmful. Well-documented cases of groundwater contamination by leachates, surface water contamination by runoff, direct contact poisoning, various forms of air pollution, and damage from fire and explosions have occurred and will continue to occur as long as unacceptable disposal practices are used. Most incidents result from open dumping of hazardous wastes on isolated tracts of land or from indiscriminate acceptance of all wastes regardless of hazard by municipal landfills.

---

*Program Manager, Hazardous Waste Management Division, U.S. EPA, Washington, DC.

For example, in 1972 eleven people in Perham, Minnesota were striken with the symptoms of arsenic poisoning. Upon investigation it was discovered that they had been drinking water from a new well that had been drilled near a 30-year-old, unmarked deposit of leftover grasshopper bait. Water samples from the well were found to contain more than 400 times the amount of arsenic maximally allowable in drinking water in the United States.

EPA's Office of Solid Waste has compiled over 400 case studies of such incidents primarily from data gathered by State environmental regulatory agencies. It is clear that open environmental abuses occur more frequently in States without such programs and without adequate documentation of damages. To this extent, the cases can be said to understate the problem.

SUBTITLE C

Subtitle C of RCRA gives EPA authority to set standards for generators and transporters of hazardous waste and for hazardous waste treatment, storage, and disposal facilities.

Subtitle C takes a pathways or "cradle-to-grave" approach to regulating hazardous waste. This means regulation of generation and transportation of hazardous waste as well as its ultimate disposition. For example, each hazardous waste load shipped offsite must be accompanied by a manifest filled out by the generator of the waste. On this manifest, the generator designates the facility to which the waste must be taken. The manifest goes with the load to the facility and the signed original is returned to the generator by the facility. This returned manifest closes the loop of responsibility for the generator. The generator is responsible for maintaining these manifests as evidence that he has properly managed his hazardous waste. National standards have been proposed for transporters that require delivery of all hazardous waste to the facility designated on the manifest. And to adequately control final disposition and prevent unsound management, facilities for treatment, storage, and disposal of hazardous waste must acquire permits.

The manifest system, the transporter standards, and the permit system should halt dumping in isolated fields and nonsecure landfills, or in muncipal sewer systems, because the generator of the hazardous waste must be able to show that the waste was sent to an acceptable, permitted facility. If attempts are made to falsify returned manifests, a cross-check with the permitted facility should quickly show that the load never reached that facility. The facilities receiving hazardous wastes must meet certain criteria for technical soundness and financial responsibility if they are to obtain permits. This prevents designation of simple pits or fields as disposal sites on manifests because such sites could never obtain permits.

Currently many sites legally accepting hazardous wastes are not environmentally suitable. Such sites include open dumps and municipal and sanitary landfills as well as "secure" landfills which were not adequately located or constructed. Under RCRA, open dumps must be upgraded to the standards for acceptable landfills or be shut down. Only chemical landfills, other land disposal techniques, and treatment facilities shall be permitted to manage hazardous wastes.

Taken together, the manifest and permitting requirements should force most hazardous wastes to appropriate management facilities at the same time they close environmentally unsound facilities, which will decrease current capacity. This should substantially increase demand for acceptable hazardous waste management.

STATE IMPLEMENTATION

The intent of Congress and the policy of EPA is to make the hazardous waste management program resulting from the Resource Conservation and Recovery Act as much a State-run operation as possible. Under the Act, the Administrator must authorize a State to operate its program in place of a Federal operation, if certain conditions are met.

To acquire full authorization, a State program must be equivalent to the Federal program under Subtitle C, be consistent with Federal programs under Subtitle C, be consistent with Federal or State programs applicable in other authorized States, and provide for adequate enforcement of compliance.

Consistency with Federal or State programs applicable in other States means consistency with other authorized programs. EPA believes the free movement of hazardous wastes between States to be an integral part of a consistent, national hazardous waste program and for this reason is considering not authorizing State programs which include bans on the importation of hazardous wastes from other States. States applying different standards to wastes originating outside the States will not be authorized.

IMPLEMENTATION PROBLEMS

There are several potential problems that must be dealt with in order to successfully implement this national hazardous waste management program. Some States may be unable or unwilling to take up the program and thus place the responsibility for implementation on the EPA regional office. Public opposition to hazardous waste management facility siting may prevent opening a new capacity and threaten continued operation of some existing capacity. Also, it will take time for the relatively small hazardous waste management industry to grow sufficiently to handle the expected volume demand. Thus, for the intervening period of indefinite length, a capacity shortfall may occur.

A State may fail to pick up the program for other reasons. It may simply lack the legislative authority to control hazardous waste. Some State legislatures meet only every 2 years; thus, even a State desiring to accept the program may experience lengthy delay in receiving the authority to do so.

Some States will lack the resources to operate a program equivalent to the Federal one. Although there will be grant money available, this must be matched at the 25 percent level by State funds which may not be available. Resources include personnel and such things as laboratory and data processing capabilities which may take time to develop even when sufficient funds are available.

Finally, some States may not agree with the regulatory program adopted by EPA and thus may choose not to meet EPA requirements for authorization. These States may, for example, ban importation of hazardous wastes from other States thus forcing each State to needlessly duplicate costly facilities to manage all wastes. Such inconsistency could prevent a particular hazardous waste from reaching the facility best able to manage it. It could also prevent the industry from realizing economies of scale present in large facilities that serve wide areas.

Public reaction to the siting of hazardous waste management facilities has been largely adverse. For example, in Wilsonville, Illinois, what the State has determined to be a technically acceptable facility has met with strong local opposition due to its proximity to the town. In general, public opposition is based on an understandable fear for health and safety and reduced property values. Most people do not want hazardous waste mangement facilities nearby although they see the need for them someplace else.

Another implementation problem is the large number of potential generators who generate relatively small quantities of hazardous waste, or who generate in an erratic fashion. Chemical containers, for example, although considered to be hazardous unless properly drained and rinsed or reconditioned, in total weight are not a significant source. Still they are ubiquitous and are generated in many areas that do not have convenient, appropriate disposal facilities. This argues, of course, for the development of methods and practical procedures that can be established in these areas to decontaminate the containers and render them fit for recycle, reuse, and the like. Retailers who occasionally break a case of chemicals or have "leakers" are another special group.

Our current approach to the retailer and other "small" generator problems has two facets. First, we identify as generators only those who produce and dispose of 100 kg of hazardous waste per month. This quantity, (about one-half drum of most liquids), excludes over half of the potential generators, but "loses" only about one-half percent of hazardous industrial wastes. Since RCRA prohibits open dumping, this small quantity will be forced to acceptable landfills that meet the Subtitle D criteria.

Secondly, we are considering relieving

retailers from the manifest reporting and recordkeeping burdens if they too dispose of waste in Subtitle D or C facilities.

There will be hazardous waste management regulations nationwide regardless of which individual States accept the program contained in RCRA. However, implementation will be slower and may be less responsive to local needs if EPA must institute the program in most or all of the States.

The ability of the hazardous waste management industry to overcome local opposition to siting and expansion activities is not clear. At the least, such influences will delay implementation of the Act. At worst, it could stymie development of necessary sound capacity, causing a serious shortfall and forcing hazardous wastes into the fields and sewers, to the detriment of both public health and the environment. In all, public opposition to siting may become the greatest obstacle to implementation of a program for sound hazardous waste management and deserves our most thoughtful concern.

Session II: WASTEWATER POLLUTION CONTROL TECHNOLOGY

W. Wesley Eckenfelder, Session Chairman

ORIGIN AND INTERNAL CONTROL OPTIONS FOR PRIORITY POLLUTANTS IN THE TEXTILE INDUSTRY

Edwin L. Barnhart*

Abstract

To date, textile industry has been able, with some minor exceptions, to meet the criteria set down for water pollution control. The industry has developed within itself the technology and methodologies necessary for the operation and control of treatment plants that achieve best practical treatment of higher levels of removal. By and large, the movement within the industry has been quite rapid and orderly.

By comparison, the introduction of priority pollutant control will cause major problems for the industry. The reasons that disruption will be caused are important to understand. The major problem is that identification and control of the priority pollutants depends on a level of chemical analysis expertise and skill which exceeds the level required by manufacturing demands of the industry. BOD's, COD's, and even the more complicated nitrogen analyses required by conventional pollution control can be performed by a skilled plant chemist, but the introduction of complex gas chromatography or gas chromatography/mass spectrometry (GCMS) exceeds the general level of background of these individuals. Further, the type and class of equipment required for these advanced analyses exceed the requirements for the normal operation of the manufacturing facilities. Although this is not true for the selected few high technology companies within the industry, the majority of the operating companies will find themselves in this situation.

In a similar manner, physical and chemical phenomena associated with the operation of a secondary or even a tertiary plant are easily comprehended by a typical plant engineer. The complexities of the systems that may be required to control priority pollutants are by nature intrinsically involved with the chemistry of the reactions and may very well require special expertise unlikely to be available within any of the smaller companies.

The textile manufacturing industry's problem is further complicated by the fact that, by and large, it does not itself manufacture the chemicals used in its reactions, nor has it been common practice for the suppliers to list, in a meaningful generic fashion, the components of the various mixtures involved. Even more fundamentally, many of the dye stuffs and other materials commonly used in the industry are not analyzed, even during their manufacture, to the point of determining the various intermediates that can exist.

The variety and complexity of the chemicals employed in an average textile manufacturing operation are somewhat mind boggling. In preparing for this paper, typical operating records for several mills were examined. During an average year, the mills examined used from 100 to 300 specified compounds. Of the compounds used about one half were identified by trade names rather than by their specific chemical formula or name. Several randomly examined trade named compounds contained from 9 to 15 components as part of the manufacturers' specifications of the particular compound. Many of the individual components either appear on the priority pollutant list or are likely to make the list as it expands. But even more importantly, the one sample of a compound that was subjected to further actual analysis showed many components not listed by the supplier. Trace amounts of a wide variety of chemical intermediates were found. These compounds also were either on the list or are subject to early inclusion. It is against this background, with an understanding that thousands of compounds, many of them unsuspected, pass through a typical textile mill in a given year, that we must consider the problem faced by the industry.

IDENTIFYING COMPOUNDS OF CONCERN

The first step of any program to control the discharge of priority pollutants must be the

---

*President, Hydrosciences, Inc., Arlington, TX.

Preceding page blank

identifications of the compounds present in the effluent. This is not always as straightforward as it would seem. For convenience, a list of the compounds presently designated as priority pollutants is presented in Table 1. The list includes 114 organic compounds, 13 heavy metals, cyanide, and asbestos. EPA is presently hard at work developing discharge standards for each of the materials for a variety of industrial categories. At present the only reasonable assumption is that each of the specific compounds will be controlled at some low level in the given effluent. Specific compounds, such as the heavy metals, and the more carcinogenic compounds may require complete removal.

Perusals of the list will quickly reveal that many of the compounds are commonplace in the textile industry. The cause or occurrence of these compounds may be generally attributed to three main factors—direct production use, indirect production use, and nonproduction use.

Direct Use

A study of chemical purchasing lists will quickly identify the chemicals of concern that are in quantity use in the facility. Although such materials as benzidine and many heavy metals are passing out of use, carbon tetrachloride, benzene, ethylbenzene, and the like will remain common chemicals for at least a foreseeable future. Materials identified through purchasing analysis can be handled in a direct manner compatible with concern.

Indirect Use

Chemicals introduced into a plant through indirect use are more difficult to detect. The first and most significant source of these materials is the so-called proprietary chemical. Where a specific functional chemical or dye is identified only by its trade name, the components of that compound must be identified by working with the manufacturer. But further, it must be noted that in many cases, even the compoundor does not really have information on the materials that are present. Heavy metals, traces of reaction intermediates, and the like are persistent in the widest variety of proprietary chemicals purchased within the industry.

Further introduction of priority pollutants may occur through nonmanufacturing uses such as materials used to preserve and stabilize as well as sprays to protect against mold, etc., and in the packaging area. A variety of phenolic type materials, for example, are used as sealants and are present in a variety of packaging schemes. Isolation of priority pollutants from such activities requires detailed investigation and is often time-consuming and frustrating. By way of example, the components of a typical carrier are listed in Table 2. A gas chromatography/mass spectrometry (GCMS) analysis of this material showed in excess of 25 discrete compounds.

Nonproduction Use

By far, the most difficult materials to control come from nonproduction uses; areas that would never have been of concern before. Examples of these contaminants include: runoff from sprays used to control shrubbery and weeds around waste treatment facilities and for general ground control, sterilizing agents used by kitchen and cleaning services, and materials employed in general construction around the plant site. At first these uses may seem trivial, but understand that in a typical manufacturing plant consuming a million gallons of water a day, 1 pound of a chemical causes a concentration in the effluent in excess of .1 mg/liter or 100 ppb. This is significantly above the level at which many of the priority pollutants will be controlled.

In a recent investigation a particular material of concern was found to be a component of a commercial cleaning solution used by contract labor over each weekend. The concentration of this material reaching the treatment plant was sufficient to contaminate the effluent for several days of the following week. This compound that "couldn't possibly be there" was only found and eliminated after a systematic, time-consuming evaluation of every possible cause.

From the above discussion, it should be clear that priority pollutants will enter a plant from the widest conceivable range of activities carried on at the plant site. Working to control these substances then must envision a much broader approach than has previously been conceived within the industry.

TABLE 1. COMPOUNDS PRESENTLY DESIGNATED AS PRIORITY POLLUTANTS

Phenols

- Phenol
- 2-Chlorophenol
- 4-Chlorophenol
- 2,4-Dichlorophenol
- 2,4,5-Trichlorophenol
- 2,4,6-Trichlorophenol
- Chlorocresol
- Pentachlorophenol
- 2,4-Dimethylphenol (xylenol)
- 2,4-Dinitrophenol
- 4,6-Dinitrocresol
- 2-Nitrophenol
- 4-Nitrophenol

Substituted aromatics

- Chlorobenzene
- 1,2-Dichlorobenzene
- 1,3-Dichlorobenzene
- 1,4-Dichlorobenzene
- 2-Chloronaphthalene
- 1,2,4-Trichlorobenzene
- Nitrobenzene
- 2,4-Dinitrotoluene
- 2,6-Dinitrotoluene
- Benzidine
- 3,3-Dichlorobenzidine
- 1,2-Diphenylhydrazine
- PCB's
- Hexachlorobenzene

Aromatic hydrocarbons

- Acenaphthene
- Benzene
- Ethylbenzene
- Fluoranthene
- Naphthalene
- Toluene
- Tetrachlorodibenzo-*p*-dioxin
- Benzanthracene
- Dibenzathracene
- Benzopyrenes
- Benzofluoranthenes
- Chrysene

Aromatic hydrocarbons (con.)

- Indenopyrene
- Anthracene
- Phenanthrene
- 1,12-Benzoperylene
- Fluorene

Organic

- Acrolein
- Acrylonitrile
- bis (chloromethyl) ether
- bis (2-chloroethyl) ether
- 2-Chloroethyl vinyl ether
- 4-Chlorophenyl phenyl ethers
- 4-Bromophenyl phenyl ethers
- bis (dichloroisopropyl ether)
- bis (2-chloroethoxy) methane
- Polychlorinated diphenyl ethers
- Isophorone
- Phthalate esters
- Vinyl chloride
- N-nitrosodimethylamine
- N-nitrosodiphenylamine
- N-nitrosodi-*n*-propylamine

Chlorinated solvents

- Carbon tetrachloride
- Chloroethanes
  - 1,2-dichloroethane
  - 1,1-dichloroethane
  - 1,1,1-trichloroethane
  - 1,1,2-dichloroethane
  - hexachloroethane
- Chloroform
- Dichloroethylene
  - 1,1-dichloro-
  - 1,2-dichloro-
- Dichloropropane
- Dichloropropene
- 1,1,2,2-tetrachloroethane
- Chloroethane (ethyl chloride)
- Methylene chloride

Chlorinated solvents (con.)

- Methyl chloride
- Methyl bromide
- Bromoform
- Trichlorofluoromethane
- Dichlorodifluoromethane
- Hexachlorobutadiene
- Hexachlorocyclopentadine
- Hexachlorocyclohexane
- Hexachloroethylene
- Tetrachloroethylene
- Trichloroethylene
- Dichlorobromomethane
- Chlorodibromomethane

Pesticides

- Aldrin + metabolites
- Dieldrin + metabolites
- Chloradane + metabolites
- Endrin + metabolites
- PCB's
- DDT + metabolites
- Endosulfan + metabolites
- Heptachlor + metabolites
- Toxaphene + metabolites
- Lindane

Metals

- Antimony (total)
- Arsenic (total)
- Asbestos (fibrous)
- Beryllium (total)
- Cadmium (total)
- Chromium (total)
- Copper (total)
- Cyanides (total)
- Lead (total)
- Mercury (total)
- Nickel (total)
- Selenium (total)
- Silver (total)
- Thallium (total)
- Zinc (total)

TABLE 2. CARRIER X

Xylene
o-Dichlorobenzene
Benzoic ester
1,2,4-Trichlorobenzene
Toluic ester
Methyl salicylate
Butyl benzoate
β-Methyl naphthalene
α-Methyl naphthalene
Diphenyl
o-Phenylphenol
Unknowns (as diphenyl)
Dimethyl phthalate

CONTROL OPTIONS

There are four options available for priority pollutant control: chemical control; contractor control; in-plant control; and treatment.

Chemical Control

Substitution—

The first and most obvious method of eliminating priority pollutant problems is the substitution of acceptable or treatable chemicals for those presently that are undesirable. As obvious as this action seems, many major companies have not yet begun a search of their purchased chemicals for this purpose. The development of alternate procedures and chemicals is a long, time-consuming job, and the sooner begun, the better the probability it will be finished in time to avoid costly treatment.

But the textile industry will never be able by itself to achieve the chemical substitutions required. Rather, the industry as a whole should request that its chemical suppliers provide alternates. The economic incentive of the market is a sufficient driving force for the large chemical companies and others to dedicate research dollars to the solution of the industry's problems. It is the industry's responsibility, however, to inform these people in a clear manner of their absolute intention to make such changes and to create the driving force.

Process Change—

Process changes to minimize or prevent pollution emissions have been an ongoing process in the textile industry for the last decade. A new mill designed under today's specifications uses 30 to 40 percent of the water that would have been considered normal usage in the recent past. Similar and possibly expanded rates of process modification will be necessary to completely close certain areas of the plant that contain priority pollutants. Zero discharge of undesirable materials should in fact be an at-

Investigations of process change require a detailed understanding of the economic alternatives and the ability to invest money in appropriate systems to eliminate long-range problems. Such studies, as in the case of chemical substitution, require significant lead time, and the industry even now should be turning its attention to these areas of control.

Studies start with a detailed material balance of the processes and require a high level of analytical interrogation of the various process streams. In virtually all cases, companies will be forced to employ a higher level of analytical technology than is presently available at the mills. This will undoubtedly call for a much higher level of participation by the companies' research groups.

Contractor Control

From the environmental point of view, employers are responsible for the activities of contractors on their site. In the past, little or no attention has been paid to the miscellaneous materials used by such people. In the future, tight specifications governing the use of environmentally related chemicals must be exercised. Contractors must be made aware of the pollution control programs carried on by the company and their activities must be closely monitored. Contractors, in this sense, include those performing everything from pest control to construction and erection. Many of these areas are particularly difficult since the contractors one deals with are small, independent individuals who are unaware of the composition of many of the products they employ. This is an area where possible broad-based industrial cooperation could lead to the evolution of satisfactory standards.

In-Plant Control

It is not the purpose of this discussion to deal with the technical details of the problem; however, it is appropriate to at least mention them considering the approaches that need to be taken.

In-plant control begins with strict regulation of water use. Virtually any compound is more easily handled in higher concentration, and increases in concentration often lead to economical recovery. Closed-loop solvent systems, recycle of appropriate waters, filtration, and reuse of streams present opportunities in virtually every mill. Particular progress can often be made if one recognizes that only certain components of a particular stream are of interest for reclamation. Consider dyeing solutions, for example. Considerable attention has been focused on the problem of dye removal. In fact, a detailed analysis of discharge from these operations shows that the principal chemicals of concern are carriers, wetting agents, dispersing agents, etc. Pursuing recovery of these products is far more practical and opens up the door to realistic reductions of pollutants.

At-source treatment is also appropriate in certain circumstances. Essentially this is the philosophy of intercepting concentrated streams before they enter the main sewer. Often a 5,000- or 10,000-gal/d stream treated at-source can eliminate the necessity of providing tertiary treatment for a million gallons a day. Such systems generally rely on adsorption or related phenomena for the containment of particular materials. In evaluating such processes, however, one must be certain to include the full cost including the disposal of the collected residues from each of the possible schemes. Fabric finishing is an excellent example of an area where at-source control is practical in many cases.

It is worthwhile to note that the textile industry has a particular advantage in the recovery of chemicals. In many industries the chemicals that are used undergo significant modification or reaction during processing. In general, the conditions of textile finishing are not sufficiently severe to modify the basic chemical structure of the materials involved in the process. Therefore, the resulting byproducts are basically the same as the starting materials involved in the process except they are reduced in concentration and contaminated with impurities. This lack of change of chemical structure should provide the basis on which recovery programs are based.

Treatment

If all else fails, a company will be faced with tertiary treatment for the removal of specific organics. To date, activated carbon and other specific adsorptive resins appear to be the most promising methods of priority pollutant control. But even these methods, in many cases, allow the pass through of specific undesirable products. Over the next several years a variety of new treatment processes will be introduced into the field to handle such problems. In virtually all cases, the processes will be complex systems with high energy requirements. Great care must be expended in choosing the appropriate device; looking in considerable detail at its ability to meet the ever-changing production mix present in this industry.

SUMMARY AND RECOMMENDATIONS

Enforcement of priority pollutant removal criteria will introduce a new era in the continuing environmental problems of the textile industry. These pressures will also introduce new opportunities for advancement among the companies wise enough to find better solutions to these problems. To be able to cope with this situation in an effective manner, the following course of action should be followed.

1. *Know Your Problem*
   The solution of any problem of this nature must be based on a fundamental understanding of the physical and chemical properties of the species we are dealing with. Detailed analysis of particular materials is a costly, time-consuming program and the temptation to bypass it is always there. However, you must clearly understand that sound fundamental information is the foundation on which any successful program must be based. Being penny-wise and pound foolish is a very costly business in the environment.

2. *Choose Your Ultimate Control System First*
   Look down the road to ultimate control of your effluent and determine what must be done to achieve that position. Then, at any point in time, do only that which is necessary to meet the instantaneous requirements of law. Do nothing incompatible with the long-range plan. In this manner, capital will not be wasted. Regulatory agencies are open to discussion of evolving regulation when a company can clearly demonstrate a long-range satisfactory plan.
3. *Use Purchasing and Technical Development to Solve Your Problems*
   As discussed above, the best solutions are based on elimination of the problem within the manufacturing process, giving this area the high priority research dollars it deserves to avoid much greater costs in capital later.
4. *Build Only as a Last Resort*
   Too often companies assaulted by environmental problems take the easy out—spending money. This satisfies the regulations for the time being and eliminates a problem; but, in the long run, the treatment plant consumes dollars every day for the rest of that plant's life. If you can use ingenuity and development rather than assuming capital and operating costs, you will be by far the winner.

CONTACT FILTRATION FOR TEXTILE WASTEWATER POLLUTION CONTROL IN POLAND

Jerzy Kurbiel, Wieslaw Zymon*

Abstract

Textile industry wastewater treated conventionally in a mechanical-biological treatment plant contains considerable amounts of refractory pollutants such as dyes, detergents, and other synthetic compounds. Beyond mechanical-biological treatment, they require further treatment by means of physicochemical processes, especially when the receiving stream is rather small and high water quality must be maintained.

INTRODUCTION

In the investigations presented in this paper the wastewater came from a textile factory with annual fabric production of 9,000,000 kg, in which the percentage participation of particular raw materials was: cotton, about 70 percent and synthetics, about 30 percent. The plant discharges about 6,000 m^3/day of concentrated wastewater coming mainly from two fabric finishing plants. Over 1,500,000 kg of organic chemical compounds and over 4,600,000 kg of inorganic chemicals are used per year in the production process.

After pH control by means of stack gases recarbonization and after primary sedimentation, textile wastewater was mixed with municipal wastewater in a 1:1 proportion or higher and was directed to the pilot plant, which contained an activated sludge unit and tertiary treatment devices.

The coagulation in a contact filter was one of the tertiary physico-chemical processes investigated within the Project PR-5-532-3 sponsored by EPA. In practice the coagulation of textile wastewaters is often applied before biological treatment, but in that case the required doses of the coagulant are very high reaching, even to 1,000 g/m^3.

CHARACTERISTICS OF CONTACT FILTERS

The contact filters were applied in practice for the first time by Minc (ref. 1) in 1954 for the treatment of water with constant and relatively small contents of suspended solids (below 150 g/m^3), including solids formed during coagulation. The basic aspects of the contact filter, usually constructed as single-medium, multilayer, upflow filters, lies in the combination of two processes in one chamber: the surface coagulation and filtration.

The surface coagulation, as opposed to the conventional process, which can be called volume coagulation, is characterized by a forming gel on the surface of solids, in this case on the grains of the filter medium. Surface coagulation has two specific properties that make it different and more favorable than volume coagulation: it is faster and the arising gel, in the form of flocs, is separated from water simultaneously with the coagulation itself. Also the required dose of coagulant is considerably reduced, at least 30 percent in comparison to conventional coagulation.

The contact filters for the treatment of municipal wastewater which have already been treated biologically were first applied in England in the early 1960's (ref. 2). England and the Soviet Union have the greatest research and practical experience in this area.

The theory of filtration has been evaluated most comprehensively during the IWSA Congress of 1966 by Minc (ref. 3) and the Congress of 1969 by Ives (ref. 4). The objective of research on the contact filtration done so far was to find a filtration bed of a perfect structure needed to create the so-called deep filtration, in which the fixing of suspended solids would take place within the whole mass of the bed along its depth. In practice the construction of such a perfect bed was only partly successful, in spite of many attempts.

In the downflow filter there is a domination of the upper layer, which fixes most of the suspended solids. Even in case of properly selected multimedia filters, the accumulation of suspended solids at the boundary of layers could be observed. However, the use of several bed layers enables the increase of the capacity of the bed, and as a result of it the filter cycle is prolonged.

---

*Cracow Technical University, Poland.

In England the "immedium filter" is used for tertiary wastewater treatment. It is an upflow contact filter with the granulation decreasing as the water flows upwards and containing the screen bounding from the top. Granulation and filter bed thickness of an immedium filter, the Boby Filter, is given in Table 1. Effectiveness of those filters operated on a full scale (ref. 4), determined by suspended solids and BOD_5 concentration in effluent, was in both cases 7 mg/h.

TABLE 1. GRAIN SIZE AND FILTER BED THICKNESS OF BODY FILTER (UK) (REF. 2)

Filter media	Filter bed characteristics Layer thickness (m)	Grain size (mm)
Gravel	0.15	40-50
Gravel	0.25	8-12
Gravel	0.25	2-3
Sand	1.58	1-2
Total thickness	2.23	

The research on the application of the contact filters for tertiary treatment of biologically treated wastewater has been carried out intensively in the Soviet Union since the mid 1960's (refs. 5,6). Table 2 shows bed characteristics and flow rate recommended by the Soviet Union for wastewater treatment. The application of contact filters for tertiary treatment of municipal wastewater has been studied also in Poland. Table 3 shows granulation and layer thickness of contact filters at the Zywiec pilot plant. This bed structure was proven best and recommended as design criteria for wastewater application (ref. 7). Removal of particular pollution parameters on contact filters operated without addition of coagulants, according to the results obtained at the Zywiec pilot plant (ref. 7) was as follows: suspended solids-up to 60 percent, BOD-28 percent, and COD-26 percent. When the coagulants were added, the removal percentage increased considerably. For the parameters listed above increase of removal averaged 36 percent, 20 percent, and 24 percent, respectively. In addition to this, 80 percent of phosphorus removal was obtained.

The filtration cycle lasted up to 72 hours, but because of oxygen depletion it was limited to 24 hours. It was proven that upgrading of conventional municipal wastewater treatment with the use of upflow contact filters is more economical than any other system with the same effectiveness with respect to the refractory pollutants, i.e., conventional coagulation.

METHODS

The range of investigations carried out on application of contact filters for tertiary treatment of mixed textile-municipal wastewater included determination of the following factors affecting the process and its effectiveness:

- the kind and dose of the coagulant on the removal of specific refractory contaminants from the wastewaters,
- the influence of variations in the pH reaction of the wastewater during coagulations,
- the possibility of increasing the coagulation efficiency by preliminary and post

TABLE 2. GRANULATION, BED THICKNESS, AND FLOW RATE RECOMMENDED FOR UPFLOW CONTACT FILTERS APPLIED IN USSR (REFS. 5,6)

Filter bed characteristics Filter media (from bottom to top)	Grain size, mm d_{min}	d_{max}	Layer thickness (m)	Filtration rate (m/h) Normal loading	Increased loading
Gravel	20	40	0.2-0.25		
Gravel	10	20	0.2-0.3		
Gravel	5	10	0.3-0.4	7-8	9-10
Gravel	2	5	0.5-0.7		
Sand	1.2	2	1.3-1.5		

TABLE 3. GRANULATION AND LAYER THICKNESS OF CONTACT FILTERS AT ZYWIEC PILOT PLANT (REF. 7)

Filter media (from bottom to top)	Grain size, mm		Layer thickness (m)
	d_{min}	d_{max}	
Gravel 1	20	40	0.2-0.25
Gravel 2	10	20	0.2-0.30
Gravel 3	4	8	0.8-1.00
Gravel 4	2	4	0.1-0.15
Sand 1	1.5	2	0.1-0.15
Sand 2	0.8	1.5	0.6-0.80
Total thickness			2.0-2.5

oxidation,

- the influence of the wastewater load expressed by refractories concentration, and
- the type of installation assuring an optimal course of the process.

For the contact filters the following factors were determined:

- filtration rate and washing flow rate, and
- grain size and depth of filtration bed.

In parallel, investigations were carried out on a laboratory and pilot scale. A schematic plan of the treatment plant comprising primary sedimentation of two separated streams, textile and municipal wastewaters, activated sludge unit for combined wastewater, and tertiary treatment facility is shown in Figure 1.

The wastewaters, after biological treatment, were coagulated by aluminum using two methods:

1. Surface coagulation on contact filters (Figure 2). The addition of coagulant salt to the wastewaters introduced from the bottom of the gravel-sand contact filter. The coagulation took place in this case directly in the filtration bed. A detailed scheme of the contact filter is shown in Figure 3.
2. Conventional coagulation in the reactor with suspended flocs is shown in Figure 4. After this process the wastewaters were filtered through a downflow anthracite-sand bed.

Supplementary test investigations were also carried out on the flow conditions of the wastewaters through filtration columns used for contact coagulation. During the investigations physico-chemical analyses of the wastewaters before and after coagulation were carried out on daily averaged samples. The results plotted on the scale of cumulated probability gave, as a rule, a straight line that proved their normal distribution.

FACTORS AFFECTING THE COAGULATION PROCESS

Influence of the Kind of the Coagulant

Three basic coagulants $FeSO_4 \times 7\ H_2O$, $FeCl_3 \times 6\ H_2O$, and $Al_2(SO_4)_3 \times 18\ H_2O$ were used. Applying $FeCl_3 \times 6\ H_2O$ and $Al_2(SO_4)_3 \times 18\ H_2O$ in the same manner, the optimum dose for removal of turbidity and color was 100 mg/liter. For $FeSO_4 \times H_2O$ the dose exceeded 200 g/m^3 in the majority of cases. Moreover, ferrous salts induced a secondary pink color. Further investigations on the coagulation process were carried out using $Al_2(SO_4)_3 \times 18\ H_2O$.

The decrease in pH within the values 7.5 to 5.8 causes an increase in color removal from the wastewaters. At the same time the preliminary oxidation by means of NaOCl with a dose up to 16 mg Cl_2/liter increases the efficiency of color removal in relation to the results obtained without preliminary oxidation as well as in relation to the oxidation itself, especially for lower pH values. The doses of the oxidant exceeding 16 mg Cl_2/liter do not give any increase in color removal, especially at coagulant doses above 200 g $Al_2(SO_4)_3 \times 18\ H_2O/m^3$.

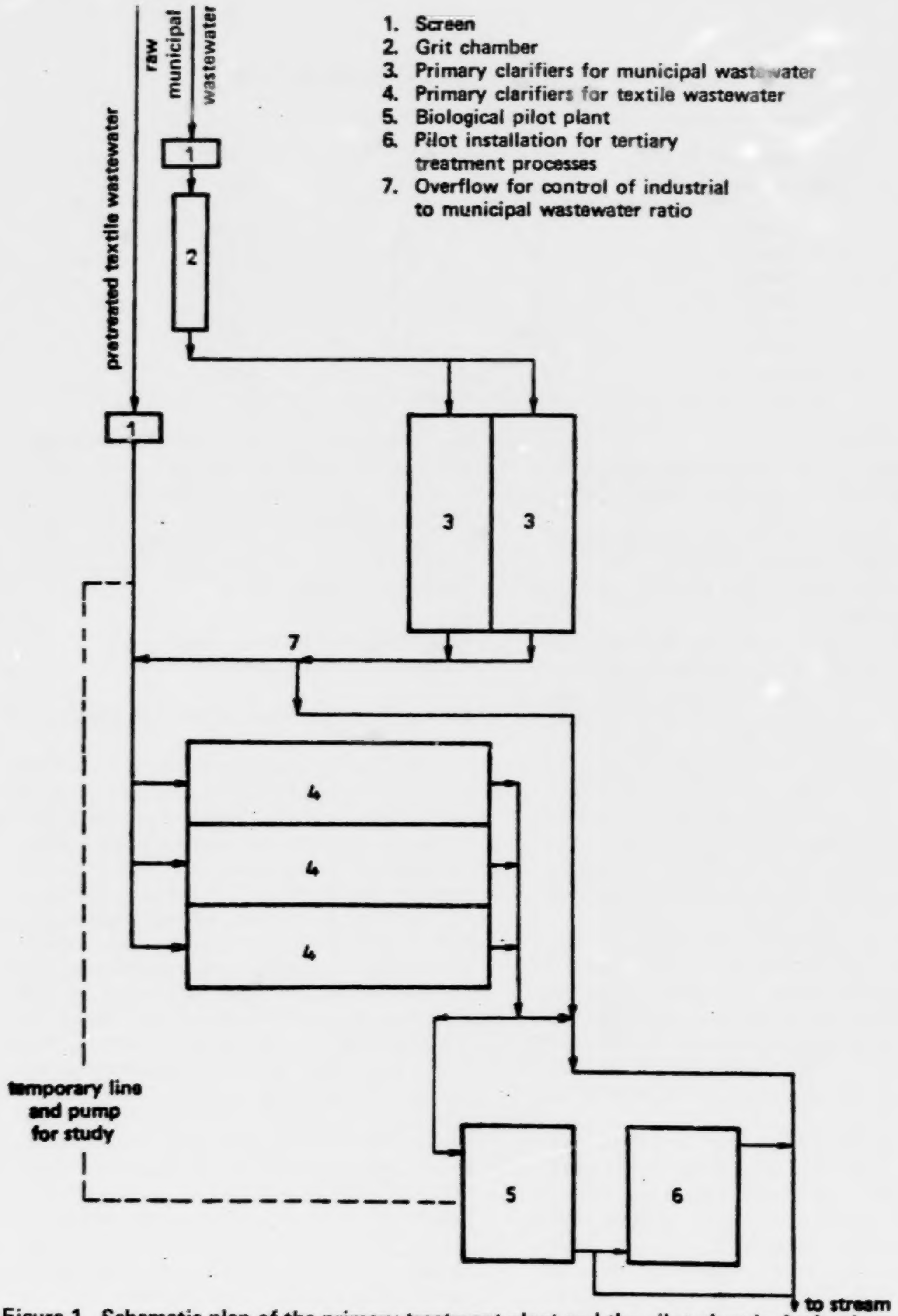

1. Screen
2. Grit chamber
3. Primary clarifiers for municipal wastewater
4. Primary clarifiers for textile wastewater
5. Biological pilot plant
6. Pilot installation for tertiary treatment processes
7. Overflow for control of industrial to municipal wastewater ratio
raw municipal wastewater
pretreated textile wastewater
1
2
1
3
3
7
4
4
4
5
6
temporary line and pump for study
to stream

Figure 1. Schematic plan of the primary treatment plant and the pilot plant in Andrychow.

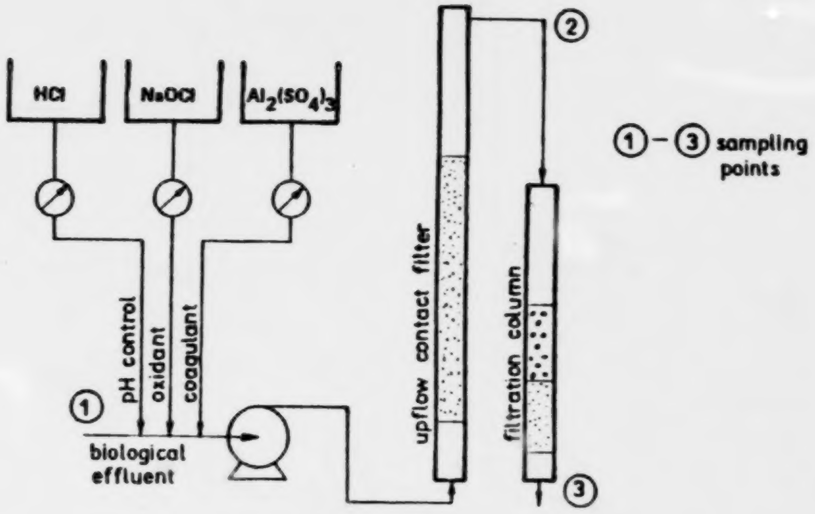


Figure 2. Schematic diagram of the pilot upflow filtration installation.

Influence of Wastewater pH, Coagulant Dose, and Preliminary Oxidation on Non-ionic Detergent Removal

A high nonionic detergent content equaling from several to more than 10 g/m^3 was found in the wastewaters after biological treatment.

Mean values from the obtained test investigation data for five wastewater samples are shown in Figure 5. From the shape of the curves the resulting speculation is that increased doses of the coagulant at a wastewater pH of between 7.4 and 6.5 cause an increase in detergent removal. At a pH of about 5.8, removal of nonionic detergents is highest, but does not depend on the dose of the coagulant when exceeding 100 mg/liter. A lower wastewater pH during coagulation causes a considerable increase in nonionic detergent removal. Investigations were also carried out with six samples of wastewaters coagulated with a dose of 200 g/m^3 at a constant pH of 6.6 and previous oxidation with various doses of NaOCl. The obtained results are represented in Figure 6. Preliminary oxidation with doses of about 5 mg Cl_2/liter gave a considerable increase in nonionic detergent removal. Increase in the oxidant doses to a value above 5 mg Cl_2/liter caused a decrease in detergent removal.

Influence of the Coagulant Dose, Wastewater pH, and Preliminary Oxidation on COD Removal

The data from the investigations presented in Figure 7 show that increase in the coagulant dose causes increase in COD removal. On the other hand, a decrease in the pH from 7.4 to 6.5 causes an increase in COD removal by about 20 percent. A further decrease in the pH to 5.8 increases the COD removal in relation to the result at a pH of 6.5 by about 10 percent. Figure 8 shows the influence of of preliminary oxidation on COD removal under a pH of 6.6 and a coagulent dose of 200 mg/liter of $Al_2(SO_4)_3 \times 18\,H_2O$. In the majority of samples, contrary to the color, the initial decrease in the COD removal was found at oxidant doses up to 10 mg Cl_2/liter. Bigger doses of the oxidant caused an increase in the COD removal. The pilot plant data have shown the positive influence of post chlorination on COD removal and the positive effect on residual aluminum in the effluent (Figure 9).

PILOT INVESTIGATIONS AND DISCUSSION OF RESULTS

Technological investigations on coagulation of a filtration bed were carried out for a number of systems that differed in construction of

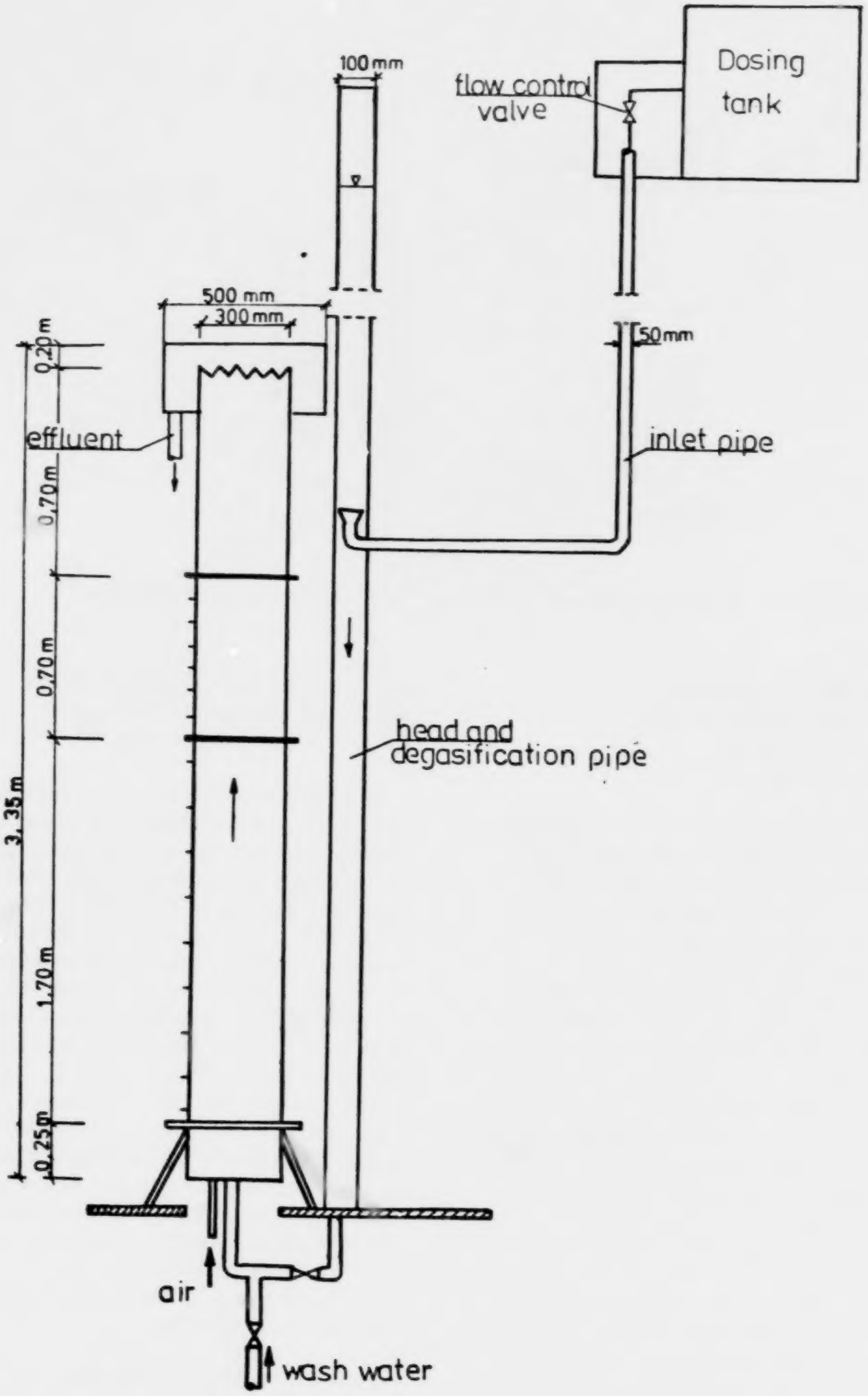
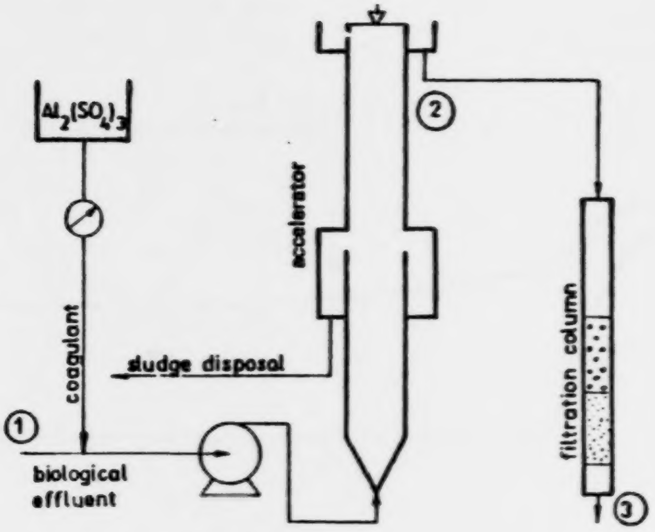

100 mm
flow control valve
Dosing tank
500 mm
300 mm
50 mm
0,20 m
effluent
inlet pipe
0,70 m
0,70 m
head and degasification pipe
3, 35 m
1,70 m
0,25 m
air
wash water

Figure 3. Experimental contact filter for tertiary wastewater treatment at Zywiec pilot plant (ref. 7).



$Al_2(SO_4)_3$
coagulant
accelerator
②
filtration column
sludge disposal
①
biological effluent
③

Figure 4. Schematic diagram of the pilot coagulation installation.

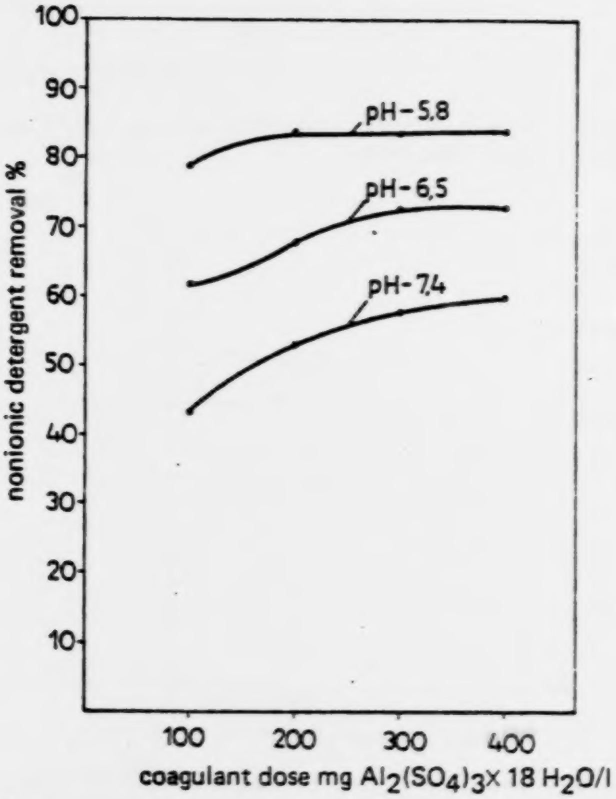


Figure 5. Average removal of nonionic detergents in relation to the coagulant dose and the pH values in wastewater.

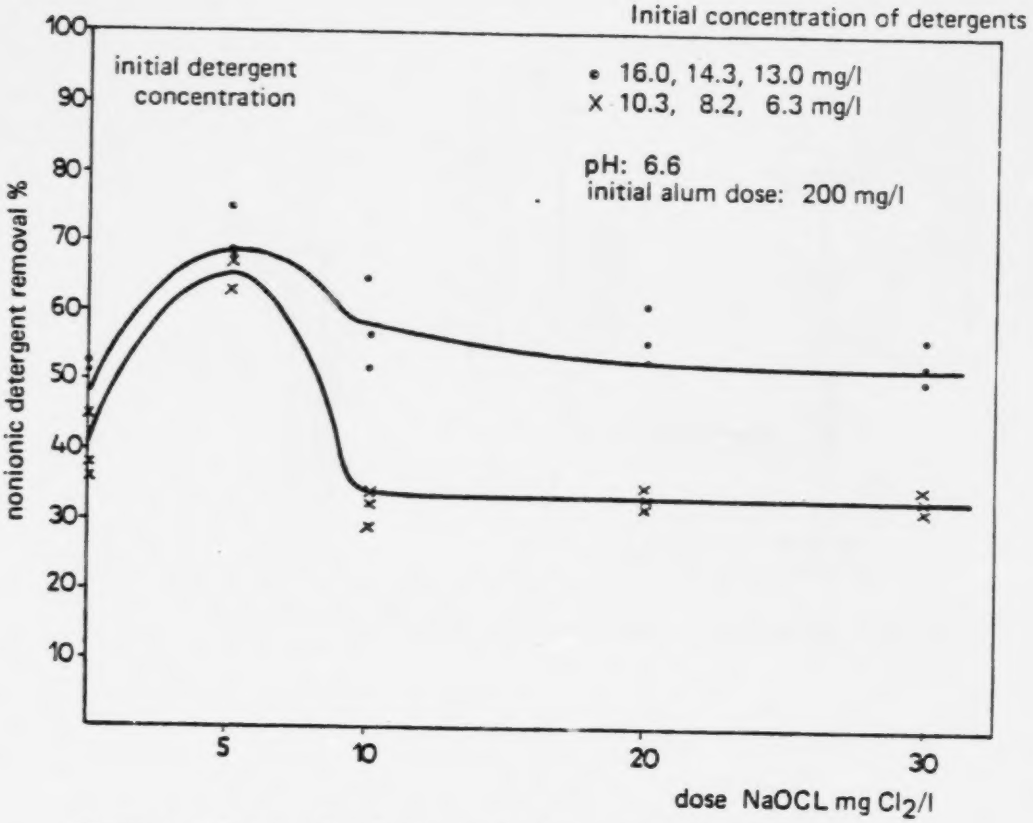


Figure 6. Influence of preliminary oxidation on nonionic detergent removal in wastewater after coagulation.

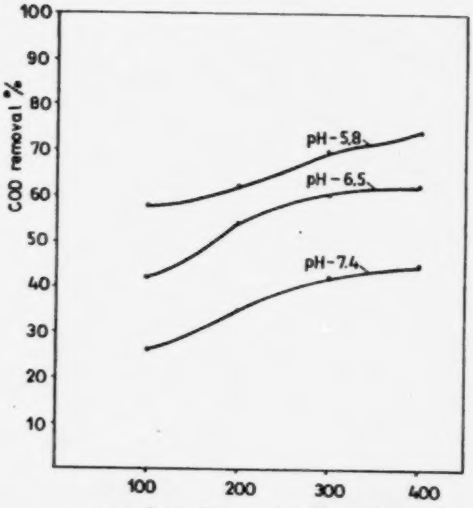


Figure 7. Average COD removal in relation to coagulant and pH value.

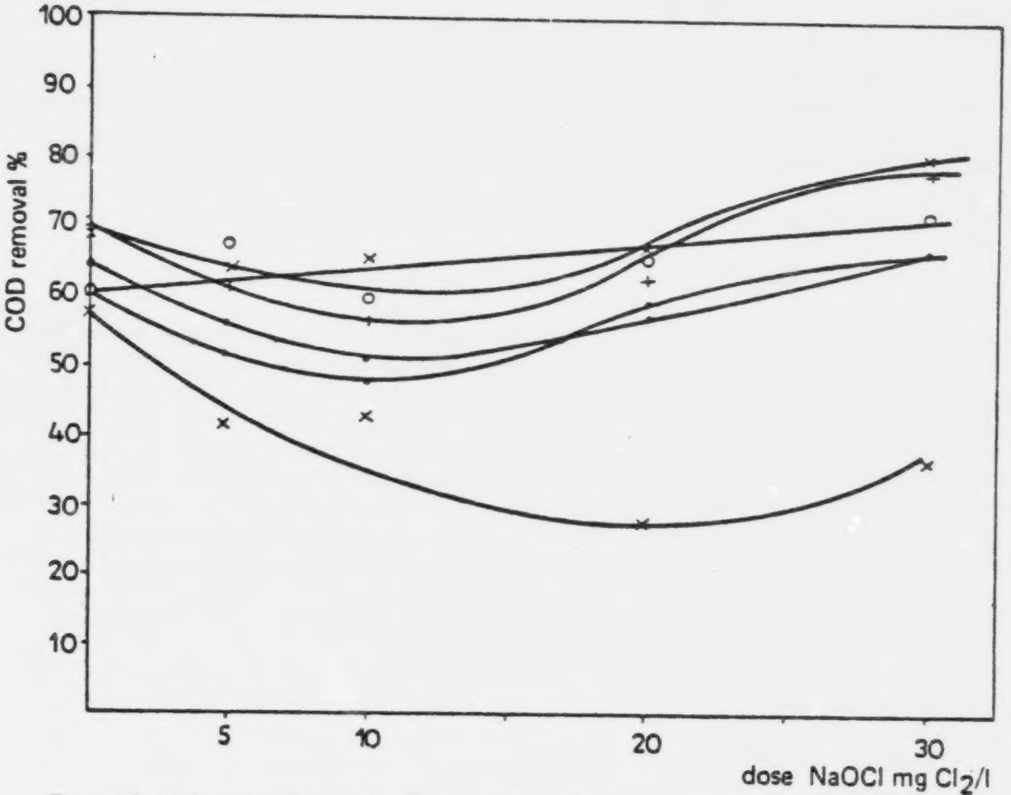


Figure 8. Influence of preliminary oxidation before coagulation on COD removal. (Tests for six wastewater samples.)

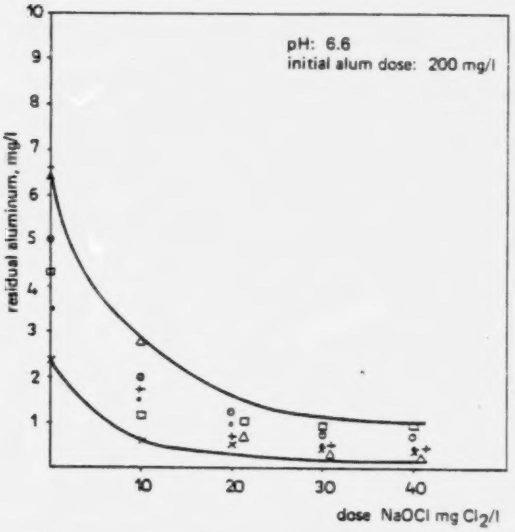


Figure 9. Influence of oxidation with NaOCl on removal of residual aluminum from coagulated wastewater.

filter media. The bed systems that gave positive results during investigations are characterized below:

System I – Structure of the filtration bed and grain size of particular layers in the system were as follows:

- height – 0.15 m, gravel depth – 2 to 4 m
- height – 1.5 m, gravel depth – 1.2 to 2 m
- height – 0.15 m, sand depth – 0.4 to 0.8 m.

The mean dose of the coagulant was up to 200 mg/liter of aluminum and the time of wastewater storage after addition of chemical compounds was about 4 minutes. The process was carried out in parallel in two columns, with the pH being lowered in one of them by means of hydrochloric acid. The average filtration cycle was about 24 hours. Table 4 presents mean results of the operation of a pilot installation for 24 days at a pH of under 6.8. The obtained results of contaminant removal were satisfactory. Removal of biodegradable organic substances was fairly great and equaled, on the average, 87 percent. Organic refractory compounds determined by COD accomplished 65 percent removal.

The influence of preliminary oxidation on the obtained treatment effectiveness is evident in Table 5. An increase higher than 10 percent was also found in color removal after preliminary oxidation of the wastewater with a dose of 10 to 14 mg Cl_2/liter at a contact time of 15 minutes.

System II – The structure of bed medium and the granular size of particle layers in this system were as follows:

- height – 0.4 m, gravel depth – 3 to 6 mm
- height – 1.3 m, sand depth – 1.2 to 2 mm
- height – 0.2 m, sand depth – 0.4 to 0.8 mm.

The applied aluminum dose equaled 250 to 270 mg/liter. In spite of a higher filtration rate the cycle was about 1 day. In this system a series of investigations was carried out by using hydrochloric acid at a decreased wastewater reaction. The wastewaters, after coagulation on contact filter, were oxidized with NaOCl with a dose of 15 to 20 mg Cl_2/liter and subsequently filtrated through an anthracite sand bed at a rate of 3 m/h. The results are presented in Table 6.

A decrease in the wastewater reaction from a pH of 7.3 to a pH of 6.8 caused a particularly evident increase in the removal of red color measured by extinction at a wavelength equal to 400 mm. Oxidation of postcoagulation wastewaters with secondary filtration caused an increase in the removal percent of all parameters.

TABLE 4. CONTAMINANT REMOVAL DURING FILTRATION WITH SIMULTANEOUS COAGULATION FOR LOWER pH (AVERAGE RESULTS BASED ON 24 DAYS OF OPERATION)

	Biologically treated effluent		Coagulated effluent		
Parameters	Average concentration	Standard deviation	Average concentration	Standard deviation	Removal (percent)
pH	7.8	0.2	6.5	0.3	
Alkalinity, meq/liter	7.8	2.2	3.4	1.6	
Permanganate COD, mg O_2/liter	18.5	7	9.2	3.6	50
COD, mg O_2/liter	72	26	25	17	65
BOD_5, mg O_2/liter	13.6	4.6	1.7	1.1	87
Suspended solids, mg/liter	32	16	13	10	56
Color, mg pt/liter	57	23	21	12	60
Color threshold	19:100	6:100	60:100	30:100	

The combined treatment system, which included the use of contact filters, was examined in order to check the combined operation and effectiveness of selected tertiary processes evaluated as optimum (Figure 10). Average effectiveness of this system for COD parameters is given in Table 7.

TABLE 5. CONTAMINANT REMOVAL DURING FILTRATION WITH SIMULTANEOUS COAGULATION APPLIED TO WASTEWATER PRELIMINARILY OXIDIZED WITH NaOCl (AVERAGE RESULTS BASED ON 28 DAYS OF OPERATION)

	Biologically treated effluent		Coagulated effluent		
Parameters	Average concentration	Standard deviation	Average concentration	Standard deviation	Removal (percent)
pH	7.7	0.2	6.4	0.4	
Alkalinity, meq/liter	8.3	3.2	3.3	1.6	
Permanganate COD, mg O_2/liter	19.0	3.5	7.9	1.3	58
COD, mg O_2/liter	80	29	22	6	72
Suspended solids, mg/liter	50	22	9	7	82
Color, mg pt/liter	56	15	17	8	70
Color threshold	20:100	7:100	69:100	31:100	
Average light absorption, E	0.093	0.040	0.030	0.026	68

TABLE 6. CONTAMINANT REMOVAL DURING FILTRATION WITH SIMULTANEOUS COAGULATION, FOLLOWED BY OXIDATION WITH NaOCl AND SUBSEQUENT FILTERING (AVERAGE RESULTS BASED ON 14 DAYS OF OPERATION)

	Biologically treated effluent		Coagulated effluent		Coagulated, oxidized and secondarily filtered			
Parameters	Average concentration	Standard deviation	Average concentration	Standard deviation	Average concentration	Standard deviation	Removal during coagulation process (percent)	Total removal (percent)
pH	8	0.2	6.8	0.3	6.8	0.3		
Alkalinity, meq/liter	8.6	1.8	4	2.2	4	2.2		
Permanganate COD, mg O_2/liter	24	6	13	3	9	3	45	62
COD, mg O_2/liter	100	25	40	13	30	10	60	70
Suspended solids, mg/liter	20	15	10	7.5	2	1.5	50	90
Average light absorption, E λ=400 nm	0.350	0.120	0.150	0.070	0.040	0.030	57	88
Average light absorption, E λ=550 nm	0.250	0.100	0.160	0.090	0.010	0.005	36	98

TABLE 7. AVERAGE EFFECTIVENESS OF THE COMBINED SYSTEM FOR COD

Kind of sample	Concentration mg O_2/liter	Removal in unit processes, in percent	Cumulative removal, in percent
Biological	100		
Contact coagulation effluent	40	60	60
After filtration and preliminary oxidation with NaOCl	30	25	70
After adsorption	6	80	94
After ozonation	5	16	95

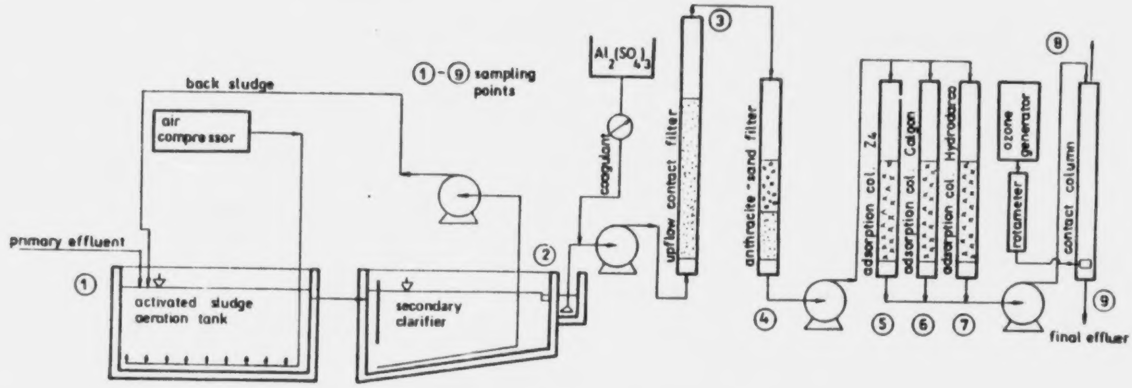

back sludge
①-⑨ sampling points
air compressor
primary effluent
①
activated sludge aeration tank
secondary clarifier
②
$Al_2(SO_4)_3$
coagulant
upflow contact filter
③
anthracite - sand filter
④
adsorption col. Z4
adsorption col. Calgon
adsorption col. Hydrodarco
⑤
⑥
⑦
ozone generator
rotameter
contact column
⑧
⑨
final effluer

Figure 10. Schematic diagram of the pilot installation for combined treatment processes.

CONCLUSIONS

- The method of surface coagulation on contact filters lends itself more to coagulation of biologically treated wastewater than conventional coagulation performed in a reactor, with suspended flocs. This is an effective and economical method of tertiary treatment.
- Preliminary oxidation before the coagulation process increases the removal of color and nonionic detergents.
- Decrease in pH produces better removal from refractory pollutants.
- Aluminum salts should be used for coagulation of wastewater, since use of ferric salts caused secondary wastewater color.
- Before the coagulation process, preliminary treatment of textile wastewater is necessary for pH control and efficient removal of biodegradable organics in the activated sludge process.

REFERENCES

1. D. M. Minc, W. P. Krisztul, and A. M. Pierlina, Mietod Kontaletnoyo Osbietleniä Wody, "Method of Contact Clarification of Water," *Sanitarnaja Technika,* Moskva, 1954.
2. G. Alpe and A. Barret, "U.K. Developments

in Upflow Titration," Fifth Federal Convention of the Australian Water and Wastewater Association, Adelaide, 1972.

3. D. M. Minc, "Modern Theory of Filtration," International Water Supply Congress, Special Subject No. 10, Barcelona, 1966.
4. K. J. Ives, "Theory of Filtration," International Water Supply Congress, Special Subject No. 7, Wien, 1969.
5. G. J. Iranijuszin, Primienienie pieszczanych filtroir na stancjoch alracji, "Application of Sand Filters at the Sewage Treatment Plants," Wodosnabzenie, *Sanitarnaja Technika*, No. 6, 1966.
6. N. A. Lukinych and B. L. Lipman, Dooczistka Gorodskich Stocznych vod na filtrach z voschodieszczim potokom, "Tertiary Municipal Wastewater Treatment on Upflow Contact Filters," Naucznye Trudy, No. 105, Ak. Ch., Moskva, 1976.
7. H. Kloss-Trebaczkiewicz, Zastosowenie filtroir kontaktozych do doczyszczania scieleow biologiernie ocryszcronych, "Application of Contact Filters to Tertiary Treatment of Biological Effluents," Doctoral Thesis, Warsaw Technical University, Warsaw, 1978.

USE OF POWDERED ACTIVATED CARBON FOR TEXTILE WASTEWATER POLLUTION CONTROL

David G. Hutton, Francis L. Robertaccio*

Abstract

Plant-scale performance tests show that the addition of powdered activated carbon to activated sludge plants treating textile wastes significantly improves effluent quality. The combined process has also been found to significantly reduce certain priority pollutants. Experience shows that the combined activated carbon-activated sludge process can be easily scaled up. Studies suggest that carbon regeneration is not required for an economically practical process, but may be suggested for improved economics and as an efficient means of sludge disposal. Performance data from Du Pont's 1.75 m^3/s (40 MGD) wastewater treatment plant treating waste from dye and textile chemicals manufacture are presented. Carbon regeneration performance will also be discussed.

INTRODUCTION

Best practicable treatment (BPT) is now well over a year behind most of us. The EPA reports that 90 percent of industry met their goal of July 1, 1977 for operation of BPT facilities. While surely there have been permit violations from time to time, the literature does not suggest any widespread problem of meeting NPDES permits for the conventional pollutants required under BPT. Most of the textile industry utilizes biological treatment, which tends to give log-normal distribution of effluent quality data for any particular plant. Hence, most plants can expect to periodically have some permit violations.

Now our thoughts turn toward coping with the provisions of the Clean Water Act of 1977. While the requirements are still in the formulation stage, it seems clear that three types of technology based effluent standards will be required on or before July 1, 1984. These are:

- Conventional pollutants – BOD, suspended solids, etc., that are now in our permits; plus, perhaps, something like total organic carbon (TOC), dissolved organic carbon (DOC), or chemical oxygen demand (COD).
- Toxic compounds – Any of the 129 specific compounds derived from the 65 classes of toxic compounds incorporated in the Clean Water Act of 1977. These are listed in Table 1, for reference.
- Nontoxic nonconventional pollutants – A third group of pollutants, which are not specifically listed as either toxic or conventional. Such pollutants may include color, turbidity, chlorides, TDS, etc.

This paper will compare the effectiveness of a combined powdered activated carbon-activated sludge treatment (Du Pont PACT[†] Process) with conventional activated sludge for all three classes of pollutants. Economics will also be discussed.

CONVENTIONAL AND NONCONVENTIONAL POLLUTANTS

Du Pont's Chambers Works

While Du Pont's Chambers Works is not a textile mill, it is a dye and textile chemical manufacturing site and has many, if not most, of the pollutants in the wastewater that one would find at a textile mill. In June 1977, Chambers Works began operation of its wastewater treatment plant to comply with best practicable technology (BPT) regulations. This wastewater treatment plant consists of neutralization and settling for primary treatment followed by combined powdered activated carbon-activated sludge (Du Pont PACT Process) for secondary/tertiary treatment. The wastewater, varying from 1.0 to 2.2 m^3/s (23 to 50 MGD) during the first year of operation, is fed to the process without equalization (Figure 1). Wastewater is pumped into the neutralizers where lime is added for neutralization. Poly-

---

*E. I. du Pont de Nemours, Inc., Wilmington, DE.

[†] Du Pont service mark for powdered activated carbon treatment.

Preceding page blank

TABLE 1. PRIORITY POLLUTANTS

Chlorinated alkanes

Methyl chloride
Methylene chloride
Methyl bromide
Chloroform
Bromoform
Carbon tetrachloride
Dichlorobromomethane
Trichlorofluoromethane
Dichlorodifluromethane
Chlorodibromomethane
Chloroethane
1, 1-Dichloroethane
1, 2-Dichloroethane
1, 1, 1-Trichloroethane
1, 1, 2-Trichloroethane
1, 1, 2, 2-Tetrachloroethane
Hexachloroethane
1, 1-Dichloroethylene
1, 2-trans-Dichloroethylene
1, 2-Dichloropropane
1, 2-Dichloropropylene
Tetrachloroethylene
Vinyl chloride
Hexachlorobutadiene
Hexachlorocyclopentadiene

Chlorinated aromatics

1, 2, 4-Trichlorobenzene
Chlorobenzene
Hexachlorobenzene
2-Chloronaphthalene
1, 2-Dichlorobenzene
1, 3-Dichlorobenzene
1, 4-Dichlorobenzene

Chlorinated ethers

bis(Chloromethyl) ether
2-Chloroethyl vinyl ether
4-Bromophenyl phenyl ether
bis(2-Chloroethoxy) methane
bis(2-Chloroethyl) ether
4-Chlorophenyl phenyl ether
bis(2-Chloroisopropyl) ether

Aromatics

Benzene
Toluene
Ethylbenzene
Naphthalene
Fluoranthene

Aromatics (con.)

Acenaphthene
Benzo(a)anthracene
Benzo(a)pyrene
Chrysene
Indeno(1, 2, 3-c, d)pyrene
3, 4-Benzofluoranthene
Benzo(K)fluoranthene
Acenaphthylene
Anthracene
Benzo(ghi)perylene
Fluorene
Phenanthene
Dibenzo(a, h)anthracene
Pyrene

Phthalate esters

bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Di-n-octyl phthalate
Diethyl phthalate
Dimethyl phthalate

Phenols

Phenol
2-Chlorophenol
2, 4-Dichlorophenol
Pentachlorophenol
2-Nitrophenol
2, 4-Dimethylphenol
4-Nitrophenol
2, 4-Dinitrophenol
4, 6-Dinitro-o-cresol
2, 4, 6-Trichlorophenol
para-Chloro-meta-cresol

Substituted aromatics

Nitrobenzene
2, 4-Dinitrotoluene
2, 6-Dinitrotoluene
2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin
Benzidine
3,3'-Dichlorobenzidene
1,2-Diphenyl hydrazine

Polychlorinated biphenyls

PCB-1242
PCB-1254
PCB-1248
PCB-1221
PCB-1232
PCB-1260
PCB-1016

Miscellaneous

Acrolein
Acrylonitrile
Asbestos
Cyanide
Isophorone
N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-n-propylamine

Pesticides

Aldrin
Dieldrin
Chlordane
4, 4-DDT
4, 4-DDE
4, 4-DDD
a-Endosulfan-alpha
b-Endosulfan-beta
Endosulfan sulfate
Endrin
Endrin aldehyde
Heptachlor
Heptachlor epoxide
a-BHC - alpha
b-BHC - beta
r-BHC(Lindane)-gamma
g-BHC - delta
Toxaphene

Metals

Antimony
Arsenic
Beryllium
Cadmium
Chromium
Copper
Lead
Mercury
Nickel
Selenium
Silver
Thallium
Zinc

electrolyte is added to the neutralizer effluent to aid in coagulating the fines prior to clarification. Primary sludge settles and thickens in the clarifiers, is pumped to storage, and finally is pumped to a filter press for concentration before disposal in a lined landfill.

Powdered activated carbon and return PACT sludge are added to the primary effluent as it is fed to the aeration tanks. Polyelectrolyte is added to the aerator effluent to aid in coagulating fines in the final clarifier. Treated effluent combines with other plant streams in a settling lagoon and is discharged to the Delaware River.

Excess PACT sludge is wasted from the aerator effluent into a thickening and storage tank. From here, the sludge is pumped to filter presses. The 40 percent solids cake obtained by filtration is then conveyed to a multiple hearth furnace where the bacteria are burned and the powdered carbon regenerated. Regenerated carbon is acid washed to prevent inert solids buildup, and then returned to the aerators. Makeup carbon is added as required.

Typically, the feed to the Chambers Works wastewater treatment plant has the composition shown in Table 2. The wastewater can be characterized as a strongly acidic, highly colored, medium strength waste. It has a low BOD/DOC ratio, suggesting a high ratio of nonbiodegradable compounds. The wastewater is somewhat brackish and has a relatively low suspended solids content.

For a portion of that year, December 14, 1977 through May 30, 1978, a laboratory activated sludge unit and a plant PACT tracking unit were run in parallel with the wastewater treatment plant (WWTP). The plant tracking unit operated at the same temperature, carbon type, and dose as the plant. For this time frame not only can plant performance be observed, but scaleup information and a comparison of PACT versus activated sludge can be obtained. A schematic of the operation during this time frame is shown in Figure 2.

BOD_5 performance is shown in Table 3 and Figure 3. The feed BOD_5 averaged 174 mg/liter, virtually the same as the primary effluent. However, as noted in Figure 3, the feed BOD_5 distribution was very peculiar, attributed to the somewhat biologically inhibitory nature of this waste, and to the inability to

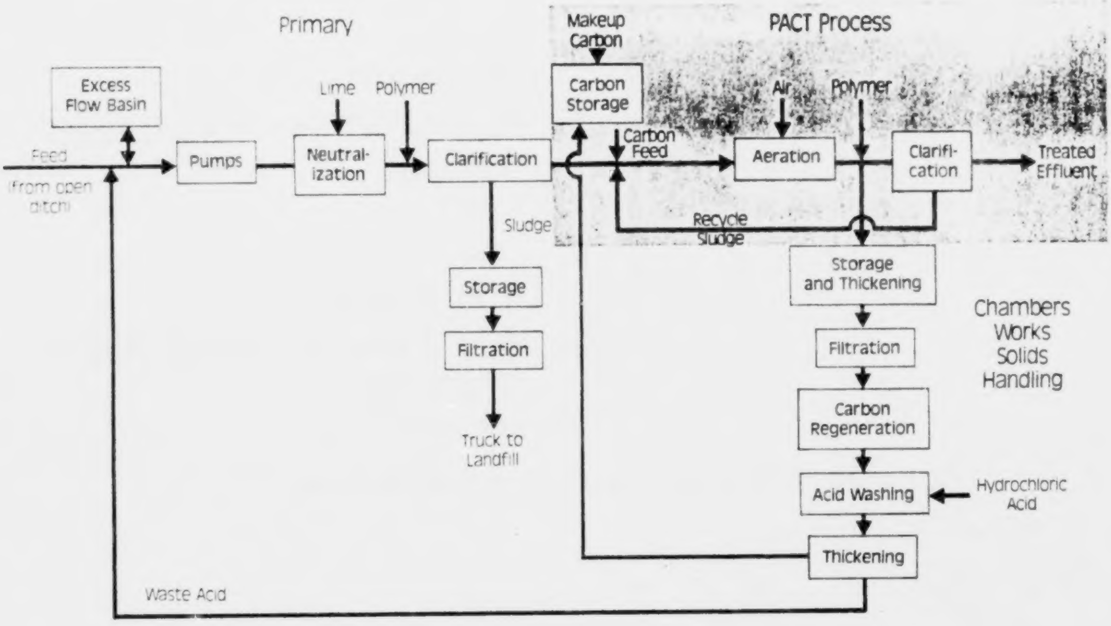

Primary
PACT Process
Makeup Carbon
Excess Flow Basin
Lime
Polymer
Carbon Storage
Air
Polymer
Feed (from open ditch)
Pumps
Neutralization
Clarification
Carbon Feed
Aeration
Clarification
Treated Effluent
Sludge
Recycle Sludge
Storage
Storage and Thickening
Chambers Works Solids Handling
Filtration
Filtration
Carbon Regeneration
Truck to Landfill
Acid Washing
Hydrochloric Acid
Thickening
Waste Acid

Figure 1. Schematic diagram of Chambers Works wastewater treatment system.

TABLE 2. CHAMBERS WORKS WASTEWATER TREATMENT PLANT FEED

	December 1977–May 1978
Flow, liters/sec	1,530 (24,200 gpm)
pH	1.98
Acidity, mg/liter	1,050
Total suspended solids, mg/liter	111
Total dissolved solids, mg/liter	3,000
Total BOD_5, mg/liter	174
DOC, mg/liter	194
Color, APHA units	1,400

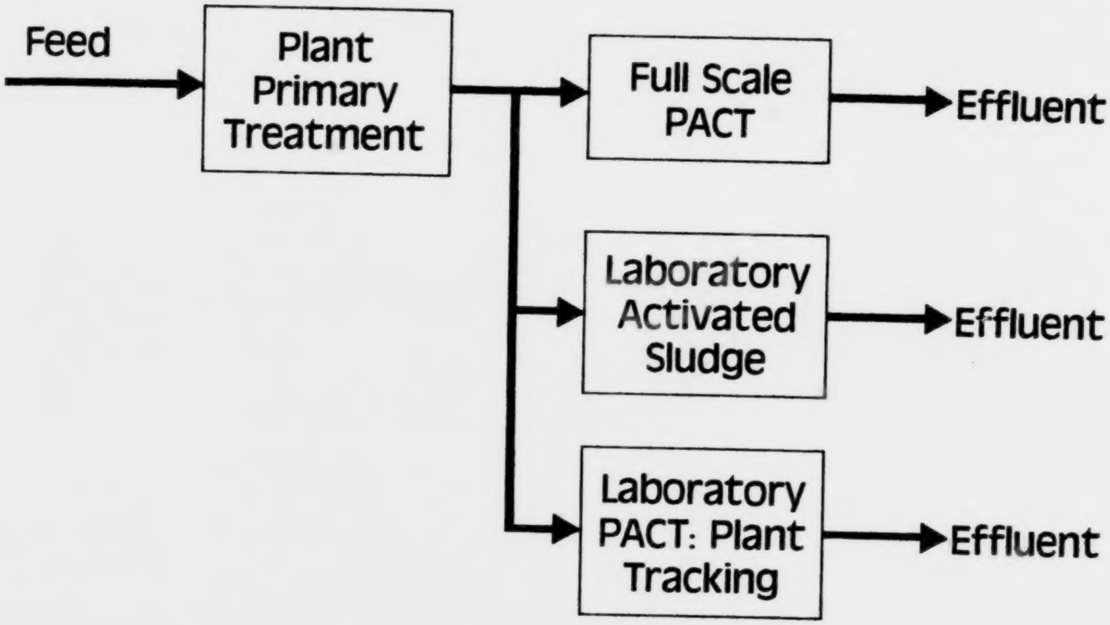

Feed
Plant Primary Treatment
Full Scale PACT
Effluent
Laboratory Activated Sludge
Effluent
Laboratory PACT: Plant Tracking
Effluent

Figure 2. Parallel operation of units at Chambers Works.

TABLE 3. CHAMBERS WORKS SOLUBLE BOD PERFORMANCE (AT ~100 PPM CARBON DOSE)

	Full Scale Treatment Plant			Lab	Lab
	Feed	Primary effluent	PACT effluent	PACT:plant tracking effluent	activated sludge effluent
No. of data points	79	115	121	76	78
Average BOD_5, mg/liter	174	175	5.1	5.0	10.3
Standard deviation, mg/liter	93	74	3.8	7.5	9.9

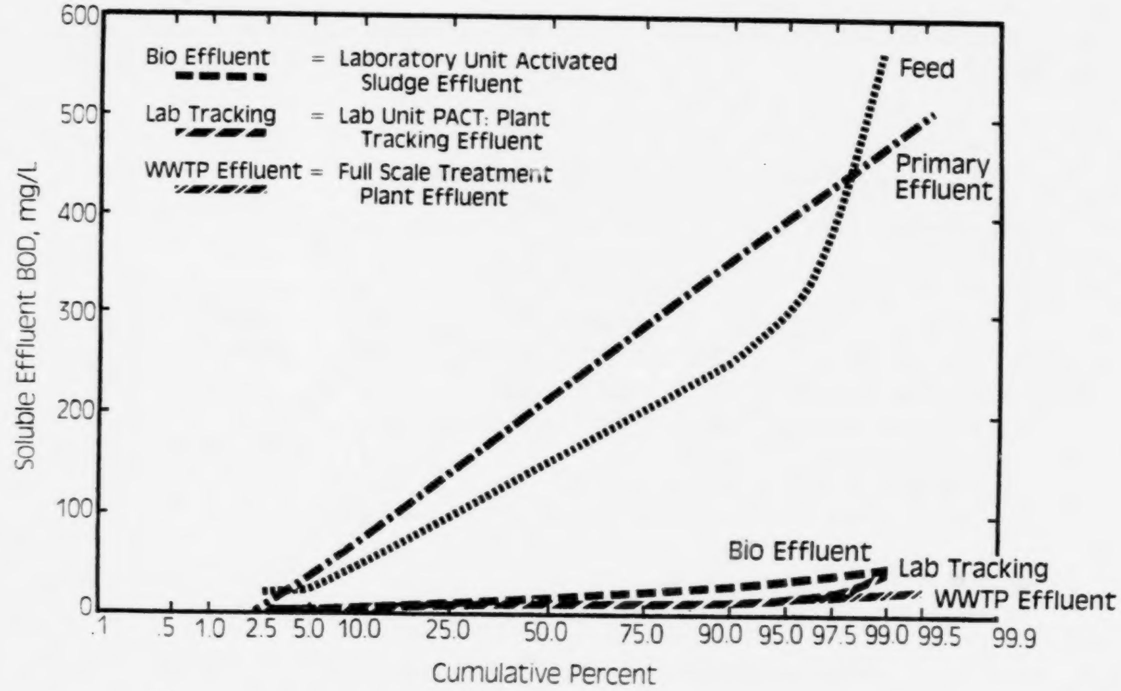


Figure 3. Chambers Works soluble BOD performance.

always get meaningful BOD_5 data. Effluent BOD_5 from the plant averaged 5.1 mg/liter versus 5.0 mg/liter from the lab tracking unit. As you can see, this represents virtually perfect scaleup from the laboratory 7-liter aerator to the plant's 45,400 m^3 (12 million gallons) of aeration. The activated sludge unit also did well during this 6-month period, but not as well as the PACT units.

Chambers Works has a stringent DOC limit in its permit, so there is a lot of interest in this parameter. As with the BOD_5 data, matched laboratory and plant data for a greater than 6-month period can be compared. Average DOC feed to the plant was 194 mg/liter, with an average effluent of 34.5 mg/liter (Table 4). Only a minor amount of DOC was removed in primary treatment. Figure 4 shows the histogram plots of the data, with the envelops showing the best log normal fit of the data. While there is some difference between the laboratory and plant results, this difference is well within one standard deviation, and is small compared to the difference between PACT and the activated sludge unit. With activated sludge alone, Chambers Works could not meet its DOC permit limit.

Chambers Works already has a permit limit for color, a nonconventional parameter. The matched laboratory and plant samples show a color increase over primary treatment and no removal of color by the activated sludge process (Table 5). The carbon addition in the PACT units effects about 60 percent color removal at the carbon dose used, which is enough for Chambers Works to meet its permit. Again the log normal distribution of data is seen in Figure 5.

Acidic Dye and Fine Chemical Manufacturer

Similar results to the above Chambers Works case were reported by ICI, United States, for a small acidic dye and fine chemical plant. Following lime neutralization, the waste was treated by a conventional extended aeration activated sludge process 817 m^3/day (0.216 MGD) design flow plant. Two carbons were tested at 85 ppm dosage levels, which resulted in equilibrium aerator carbon levels of 1,700 mg/liter. The carbon addition improved both COD and phosphorus removal (Table 6), compared to the control (ref. 1).

Eastern Pennsylvania Municipality (ref. 6)

Tests of carbon addition were conducted at an eastern Pennsylvania municipality that

TABLE 4. CHAMBERS WORKS DOC PERFORMANCE
(AT ~100 PPM CARBON DOSE)

	Full Scale Treatment Plant			Lab PACT:plant tracking effluent	Lab activated sludge effluent
	Feed	Primary effluent	PACT effluent		
No. of data points	183	192	198	177	175
Average DOC, mg/liter	194	186	34.5	29.0	61.5
Standard deviation, mg/liter	35.2	30.5	9.4	8.7	15.2

TABLE 5. CHAMBERS WORKS COLOR PERFORMANCE
(AT ~100 PPM CARBON DOSE)

	Full Scale Treatment Plant			Lab PACT:plant tracking effluent	Lab activated sludge effluent
	Feed	Primary effluent	PACT effluent		
No. of data points	119	142	153	165	160
Average color, APHA	1,130	1,410	460	420	1,410
Standard deviation, APHA	410	450	180	190	490

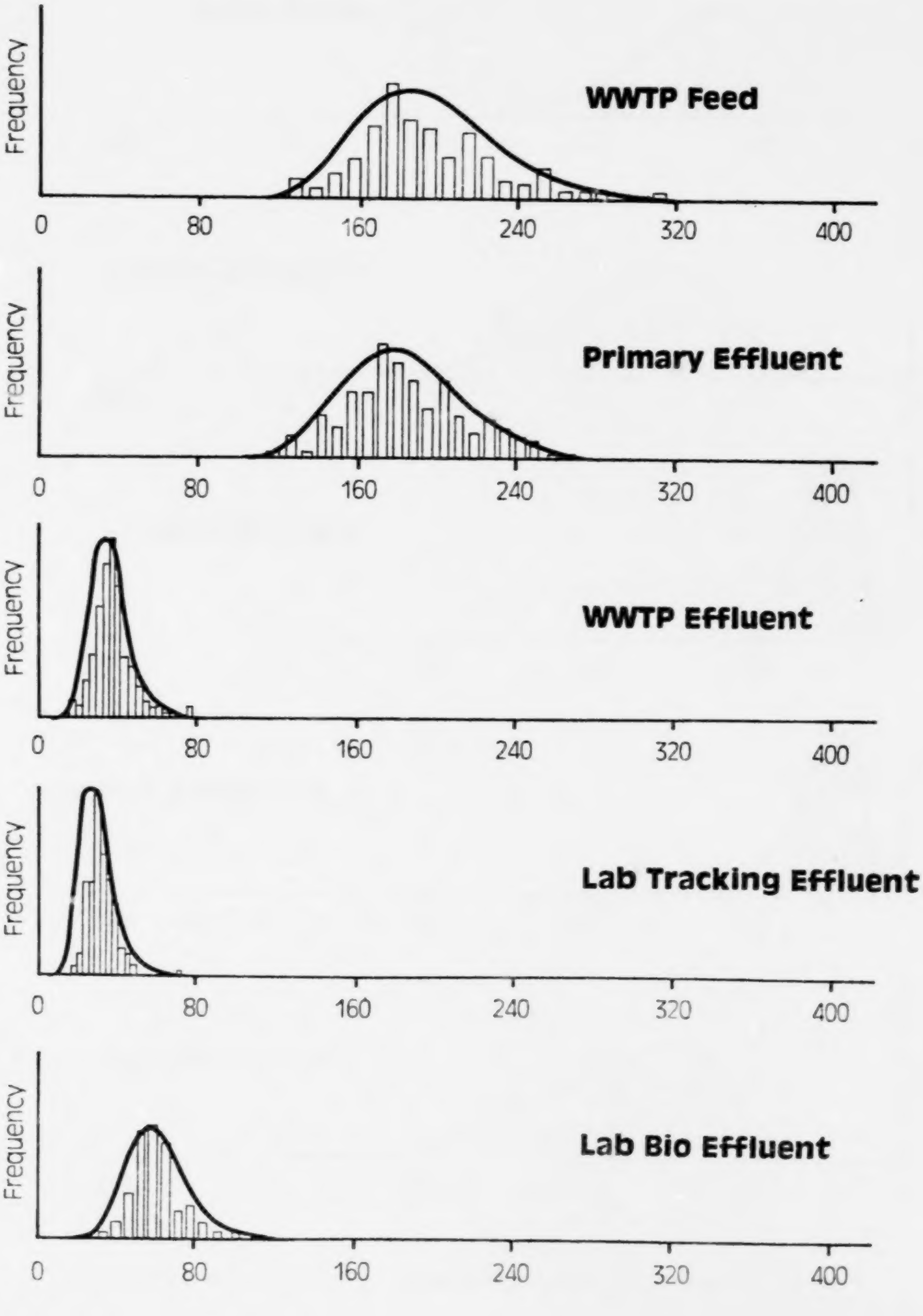


Figure 4. Chambers Works dissolved organic carbon performance (concentrations in mg/l).

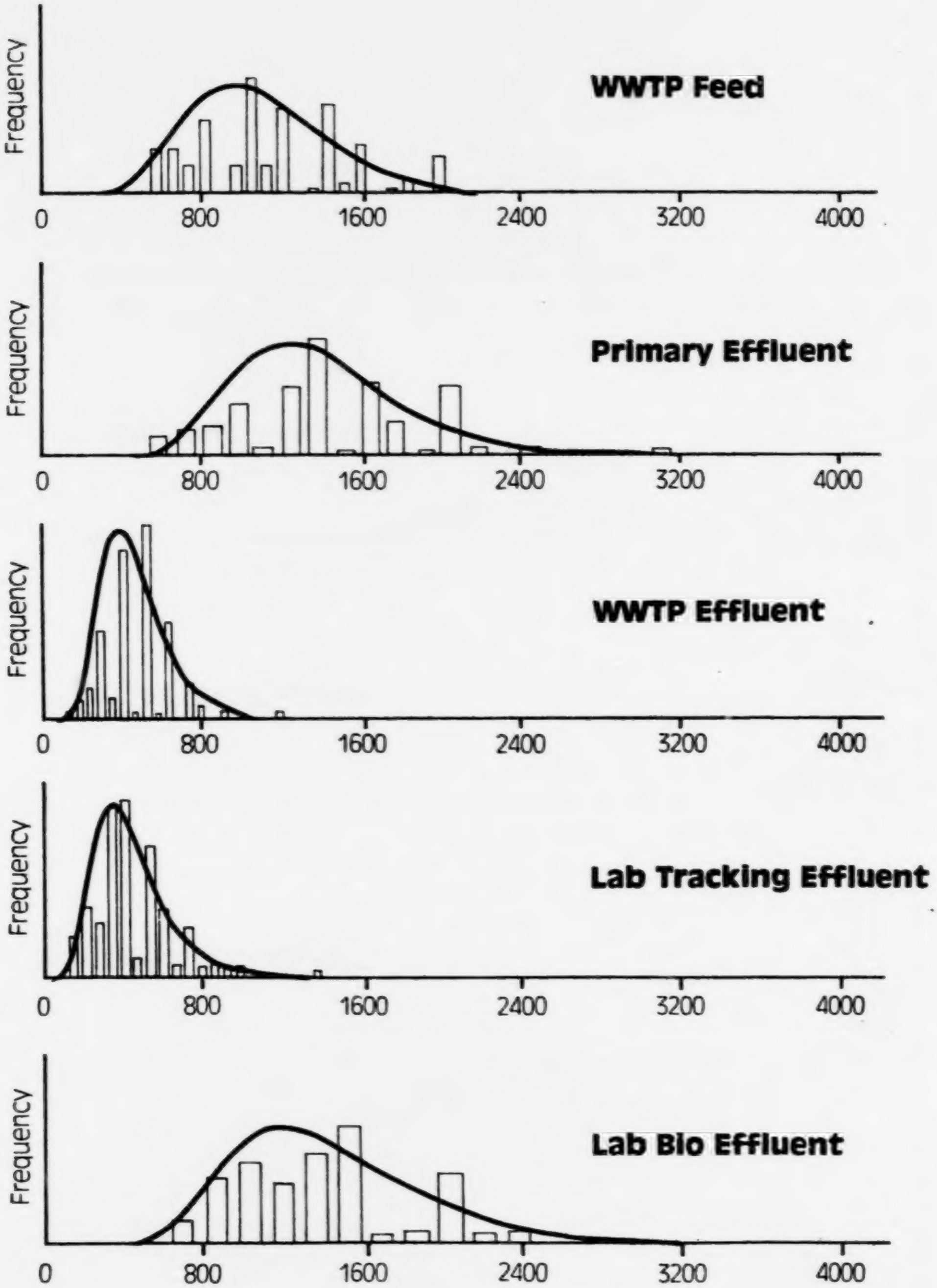


Figure 5. Chambers Works color performance (concentrations in mg/l).

TABLE 6. EFFECT OF CARBON ADDITION TO ACIDIC DYE AND FINE CHEMICAL MANUFACTURER WASTE*

	"Hydrodarco C"	"Hydrodarco H"	Control
Average flow, m^3/day	530	318	530
Average food/microorganism	.42	.15	.42
Aerator detention, hours	69	114	68
Average influent COD, mg/liter	1,106	774	1,585
Average effluent COD, mg/liter	672	332	1,155
Average percent COD removed	39	57	27
Average effluent SS, mg/liter	39	30	76
Average influent P, mg/liter	13	4	21
Average effluent P, mg/liter	2.7	0.6	12
Average percent P removed	79	85	43

*Reference 1.

TABLE 7. COMPARISON OF METALS REMOVAL AT CHAMBERS WORKS*

	WWTP feed	Primary effluent	Plant PACT effluent
Cadmium, μg/liter	19.5	7.4	6.5
Chromium, mg/liter	0.31	0.04	0.02
Copper, mg/liter	0.39	0.16	0.05
Lead, μg/liter	252	32	21
Mercury, μg/liter	0.51	<0.1	<0.1
Nickel, mg/liter	0.12	0.08	0.06
Zinc, mg/liter	1.38	0.52	0.32

*Full-scale treatment plant.

received 70 percent of its feed from a textile dyeing and finishing mill. A principal problem at this plant was overloading, with daily average flows from 0.03 to 0.08 m^3/s (0.75 to 1.8 MGD) and peaks to over 0.09 m^3/s (2 MGD) in a plant designed for 0.045 m^3/s (1 MGD). Powdered carbon additions of from 20 to 25 ppm, resulting in aerator concentrations of 900 mg/liter, increased BOD removals from 70 percent to 90 percent (Figure 6).

PRIORITY POLLUTANTS

Metals

The studies of Dyes Environmental and Toxicology Organization, Inc. suggest that a number of metals are found in the textile industry. Du Pont's Chambers Works has some of these in its wastewater, where removal by primary treatment and the PACT process can be observed. As seen in Table 7, good removal of all metals was obtained. It is to be noted, however, that most of the metals removal is accomplished by lime neutralization to pH 7.0. In all cases the metal removal is governed by the final solubility, with neither activated sludge nor carbon being particularly effective for adsorbing metals.

Nonmetals

Chambers Works has a lot of data on removal of phenols from wastewater. This is not C_6H_5OH, as measured by gas chromatography/mass spectrometry (GCMS), but phenolics as

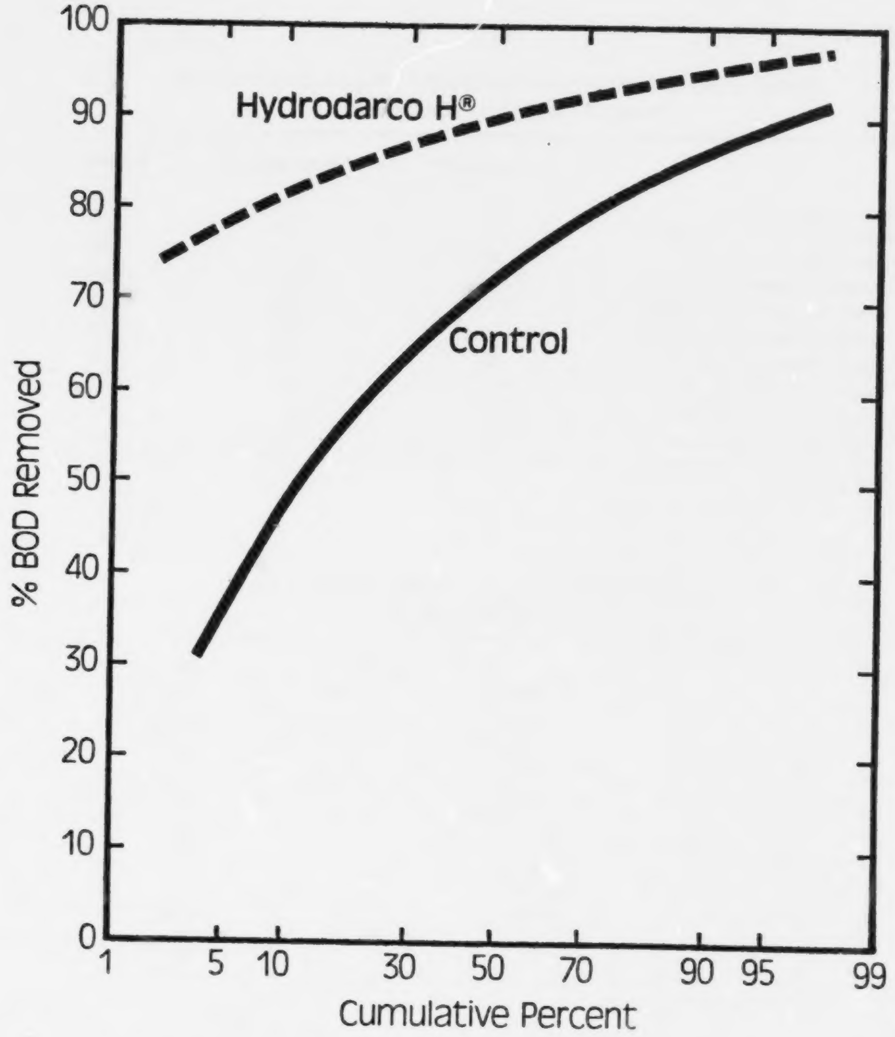


Figure 6. Effect of powdered carbon on BOD removals.

measured by ASTM Method 510, a class test. As seen in Figure 7, the Chambers Works Wastewater Treatment Plant gives 95 percent removal of phenolics, with a residual phenolics concentration about 20 percent less than that seen by activated sludge. Phenolics are basically quite biodegradable, and the difference between PACT and activated sludge may not be significant.

For other organic priority pollutants Chambers Works has some data on removal, as indicated in Table 8. Excellent removals by PACT have been observed. In addition, a 99 percent removal of acrylonitrile by the PACT process was observed in a laboratory study.

Berndt and Polkowski (ref. 3) report on the comparison of activated sludge and PACT with air oxidation for carbon regeneration (Table 9). The improved removal of PACT is readily seen. In this scheme it is reasonable to expect that individual priority pollutants can be collected at the source, co-fed with PACT sludge to the regeneration unit, and destroyed.

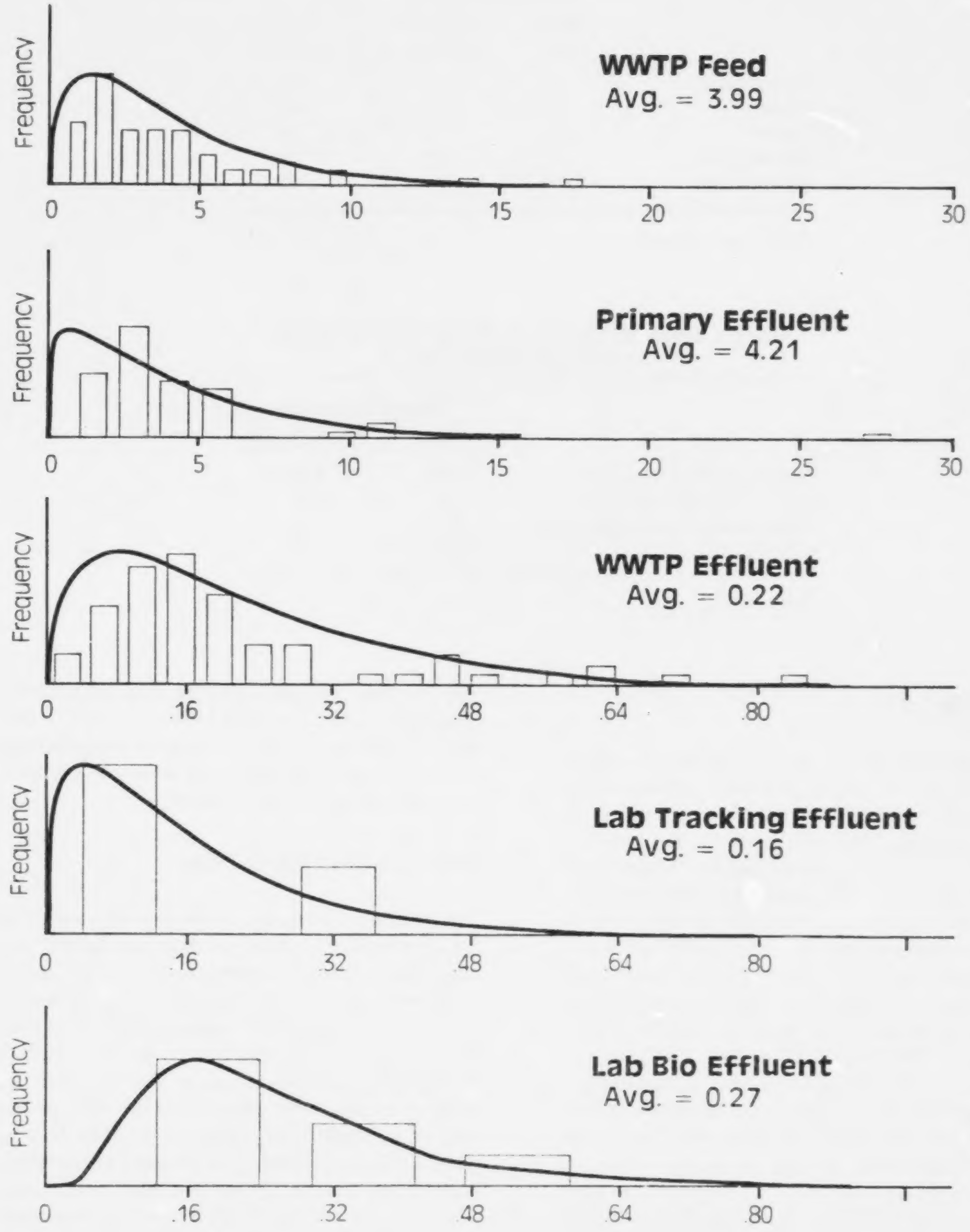


Figure 7. Chambers Works phenolics performance (concentrations in mg/l).

TABLE 8. REMOVAL OF ORGANIC PRIORITY POLLUTANTS BY PACT PROCESS AT CHAMBERS WORKS

	Concentration in ppb		
	WWTP feed	WWTP effluent	Percent removal
4-Nitrophenol	56	N.D.*	>99
Phenol	440	17.7	96
Toluene	680	4.1	99
Ethylbenzene	29	6.5	78
Chlorobenzene	1,900	12	99

*N.D. = not detectable.

TABLE 9. COMPARISON OF PACT AND ACTIVATED SLUDGE FOR ORGANICS REMOVAL*

	Effluent concentration	
Organic	PACT	Activated sludge
Chlorinated pesticides, mg/liter	0.017	0.35
Organo-sulfur pesticides, mg/liter	0	15.0
Organo-phosphate pesticides, mg/liter	1.23	3.03
PCB's, mg/liter	0.008	0.13

*Reference 3.

ECONOMICS

Culp and Shuckrow (ref. 4) did an extensive economic study that compared, among other processes, the cost of a 0.44-m^3/s (10-MGD) activated sludge and a PACT process with wet air oxidation for carbon regeneration. While these economics were for a municipal plant with extensive primary treatment, the primary treatment investment can be split out to give the comparison shown in Table 10. For reference, the Chambers Works PACT process cost about \$26 million (\$159 per m^3/day at 151,400 m^3/day capacity or \$602,000/MGD at 43.2 MGD capacity). Thus the PACT process cost, including carbon regeneration, is 25 percent above a conventional activated sludge process, and 7 percent above a nitrifying activated sludge process. They projected the cost of the carbon feed system at \$207,000 for the 0.44-m^3/s (10-MGD) plant, including engineering, interest, etc.

Operating costs were also projected for a 0.44-m^3/s (10-MGD) municipal wastewater treatment plant (Table 11). In this case it was not possible to split out the cost of primary treatment. On an overall basis, the PACT process costs were 15 percent higher than conventional activated sludge and 6 percent higher than nitrifying activated sludge.

CARBON REGENERATION

A primary question often asked about the PACT process is: Can you regenerate the carbon? The immediate response to this is: Do the economics justify it? Nearly everyone has a wastewater treatment system already, most likely a biological treatment. Anyone with a biological system has a sludge disposal system. Adding carbon very likely will not add to the volume of sludge, only the dry weight. Hence, the PACT sludge can be processed in the same manner as the activated sludge. In fact, experience shows that PACT can be processed more easily.

In a study Chambers Works did for the petroleum industry, carbon addition to an existing activated process at a dosage of 75 ppm

TABLE 8. REMOVAL OF ORGANIC PRIORITY POLLUTANTS BY PACT PROCESS AT CHAMBERS WORKS

	Concentration in ppb		
	WWTP feed	WWTP effluent	Percent removal
4-Nitrophenol	56	N.D.*	>99
Phenol	440	17.7	96
Toluene	680	4.1	99
Ethylbenzene	29	6.5	78
Chlorobenzene	1,900	12	99

*N.D. = not detectable.

TABLE 9. COMPARISON OF PACT AND ACTIVATED SLUDGE FOR ORGANICS REMOVAL*

	Effluent concentration	
Organic	PACT	Activated sludge
Chlorinated pesticides, mg/liter	0.017	0.35
Organo-sulfur pesticides, mg/liter	0	15.0
Organo-phosphate pesticides, mg/liter	1.23	3.03
PCB's, mg/liter	0.008	0.13

*Reference 3.

ECONOMICS

Culp and Shuckrow (ref. 4) did an extensive economic study that compared, among other processes, the cost of a 0.44-m^3/s (10-MGD) activated sludge and a PACT process with wet air oxidation for carbon regeneration. While these economics were for a municipal plant with extensive primary treatment, the primary treatment investment can be split out to give the comparison shown in Table 10. For reference, the Chambers Works PACT process cost about $26 million ($159 per m^3/day at 151,400 m^3/day capacity or $602,000/MGD at 43.2 MGD capacity). Thus the PACT process cost, including carbon regeneration, is 25 percent above a conventional activated sludge process, and 7 percent above a nitrifying activated sludge process. They projected the cost of the carbon feed system at $207,000 for the 0.44-$m^3$/s (10-MGD) plant, including engineering, interest, etc.

Operating costs were also projected for a 0.44-m^3/s (10-MGD) municipal wastewater treatment plant (Table 11). In this case it was not possible to split out the cost of primary treatment. On an overall basis, the PACT process costs were 15 percent higher than conventional activated sludge and 6 percent higher than nitrifying activated sludge.

CARBON REGENERATION

A primary question often asked about the PACT process is: Can you regenerate the carbon? The immediate response to this is: Do the economics justify it? Nearly everyone has a wastewater treatment system already, most likely a biological treatment. Anyone with a biological system has a sludge disposal system. Adding carbon very likely will not add to the volume of sludge, only the dry weight. Hence, the PACT sludge can be processed in the same manner as the activated sludge. In fact, experience shows that PACT can be processed more easily.

In a study Chambers Works did for the petroleum industry, carbon addition to an existing activated process at a dosage of 75 ppm

TABLE 10. INVESTMENT FOR 10 MGD MUNICIPAL SECONDARY WASTEWATER TREATMENT PLANTS (SECONDARY ONLY)*

	PACT with wet air oxidation	Activated sludge (conventional)	Activated sludge (nitrification)
Secondary treatment, $ thousands	6,388	5,124	5,986
Investment			
$ Per m^3/day	169	135	158
$ Per MGD	639,000	512,000	599,000

TABLE 11. OPERATING COST FOR 10 MGD MUNICIPAL WASTEWATER TREATMENT PLANT (INCLUDING PRIMARY TREATMENT)*

	PACT with wet air oxidation	Activated sludge	Nitrifying activated sludge
Total annual operating cost, (in thousands of dollars)	1,580	1,380	1,500
Dollars/m^3 treated	0.114	0.100	0.108
Dollars/million gallons treated	433	378	410

*Reference 4.

(75 pounds of carbon added per million pounds of wastewater treated) was assumed. At a 30 percent carbon yield loss during regeneration, the carbon value alone could not justify carbon regeneration at plant scales below 0.88 m^3/s (20 MGD). Even then, only a 10 percent net return on investment was achieved, or a payout time of 5 years.

On the other hand, carbon regeneration can be very attractive if it also serves as a means of ultimate disposal of bacterial sludge. Any of several methods can be utilized to regenerate carbon from waste PACT sludge. Chambers Works has evaluated four methods: wet air oxidation, multiple hearth furnace, transport reactor, and fluidized bed. The high temperature methods appeared to be more rigorous when the Chambers Works plant was designed. However, recently laboratory tests with wet air oxidation have produced a satisfactory regenerated carbon.

Chambers Works chose multiple hearth furnace regeneration, and installed a 5-hearth furnace 7.6 meters (25 ft) in diameter. While a lot of problems with sludge handling, particularly feeding, have hampered demonstration of what the multiple hearth furnace can do, one thing is clear; powdered carbon from the PACT process can be regenerated. Chambers Works is able to dispose of its waste biological solids, and has been able to recycle regenerated carbon. Data from the period February through June 1978 from the Chambers Works furnace are shown in Table 12. As the furnace in-time increases, the carbon recovery is expected to increase. The carbon properties from the mixed carbons being regenerated are very near one of the carbons being purchased (Table 13). Thus, the regenerated carbon quality is satisfactory.

From February through June 1978, carbon purchases averaged 111 percent of that projected in the technical manual for the wastewater treatment plant. A lower carbon dosage requirement compensates for the low regenerated carbon yield. Within the next year

TABLE 12. CHAMBERS WORKS CARBONS REGENERATION EXPERIENCE

Regeneration furnace in time, hours/day	16.6
Average feed rate, tons/day of dry solids	18.5
Carbon recovery, in percent	58

TABLE 13. CHAMBERS WORKS REGENERATED CARBON PROPERTIES

	Regenerated carbon	Virgin carbons		
		Type A	Type B	Type C
Decolorization index	12.9	21.5	15	13.6
Iodine number	514	983	504	581

Chambers Works may be purchasing less carbon than expected when the plant was designed.

CONCLUSION

In conclusion, full-scale plant tests show that the combined powdered activated carbon-activated sludge process (PACT process) not only does better than activated sludge on removing conventional pollutants (BOD, DOC, etc.), but is also more effective at removing nonconventional pollutants such as color. The PACT process can remove many metals to low levels. Preliminary results show that the PACT process is also very effective for removing some organic priority pollutants. PACT process carbon can be regenerated if economics justify the investment.

REFERENCES

1. "Powdered Hydrodarco Activated Carbons Improve Activated Sludge Treatment," ICI United States Bulletin PC-4, October 1972.
2. Alan D. Adams, "Carbon Adsorption Aids Activated Sludge Treatment at Dyeing and Finishing Plants," *American Dyestuff Reporter*, Vol. 65, No. 4, pp. 32, 34, 36, and 38, 1976.
3. Craig L. Berndt, and L. B. Polkowski, "Pact Upgrades Wastewater Treatment," *Water & Wastes Engineering*, pp. 48-50, May 1978.
4. Gordon L. Culp, and A. L. Schuckrow, "What Lies Ahead for PAC," *Water & Wastes Engineering*, pp. 67-74, February 1977.

ACTIVATED CARBON ADSORPTION FOR TEXTILE WASTEWATER POLLUTION CONTROL

E. J. Schroeder, A. W. Loven*

Abstract

Carbon adsorption technology may be utilized for advanced wastewater treatment to improve the effluent quality beyond what can generally be achieved with biological treatment and to treat wastewaters not amenable to biological treatment. Carbon adsorption is primarily effective for the removal of dissolved organic materials and, therefore, will reduce the concentration of such parameters as biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and specific organic constituents. Carbon adsorption processes will likely play an important role in future treatment systems in the removal of toxic pollutants as well as conventional pollutants.

INTRODUCTION

Full-scale carbon adsorption systems are now being utilized in several municipal and industrial wastewater pollution control applications. Carbon adsorption technology has been successfully utilized and proven in the wastewater pollution control field, and although it is not effective in all cases, it is capable of removing a wide range of organic pollutants. Its major disadvantage has been cost (dollars per pound of pollutant removed) as compared to biological treatment. Therefore, carbon processes are generally used only when specific effluent requirements justify the greater expenditure, biological treatment does not work, or if it is economical to reuse the treated effluent.

Currently there are few waste treatment installations reported with full-scale carbon adsorption processes in the textile industry as compared with such industries as organic chemicals, dye manufacturing, and pesticides. However, there have been several extensive studies and experimental programs on carbon adsorption processes in the treatment of textile wastewaters and a good understanding has emerged concerning application and effectiveness. It should be understood that the textile industry has a wide variety of manufacturing processes that contribute to significantly different wastewater characteristics among the plants even in a similar category. Also the large variety of dyes, sizing agents, dispersing agents, finishing materials, etc. have an influence on wastewater characteristics. These waste characteristics definitely impact on the treatment effectiveness and economic feasibility of carbon adsorption systems.

CARBON ADSORPTION PROCESSES FOR WASTEWATER TREATMENT

With the present state of the technology and economic factors, there are two basic types of carbon adsorption treatment processes that may be considered for end-of-pipe application with textile waste treatment; granular activated carbon adsorption (GAC), and powdered activated carbon (PAC) with activated sludge. Each of these processes has certain advantages which should be tested and evaluated for a particular application.

GRANULAR ACTIVATED CARBON ADSORPTION

A typical treatment scheme utilizing a GAC tertiary treatment system (i.e., following activated sludge secondary treatment) is shown in Figure 1. A multimedia filter (MMF) is recommended prior to the GAC columns to reduce the concentration of total suspended solids in the influent to the GAC system. The lower total suspended solids concentration allows the GAC system to perform more efficiently by not "blinding" the carbon surface. The MMF also provides protection for the GAC unit in the event of an upset in the biological treatment system which might result in a shock loading to the GAC system of total suspended solids

---

*Engineering Science, Inc., Atlanta, GA.

being discharged from the secondary clarifier.

For illustration purposes a conceptual process flow diagram of a 2-stage, countercurrent pressure downflow GAC system is shown in Figure 2. This system consists of three adsorber units, a backwash sump, and influent and backwash pumps. In this scheme the adsorbers are operated with two units in series and the third adsorber as a standby unit. When the carbon is exhausted in the first adsorber it is taken out of service and the standby unit is placed in the number two series position. The exhausted adsorber is charged with regenerated or virgin carbon and then assumes the standby position. The GAC effluent is discharged to a backwash sump before final discharge. The backwash sump serves as a reservoir of water for backwashing the adsorbers. Backwash water containing carbon fines and other suspended solids is discharged into the biological system.

Carbon regeneration can be provided offsite through a regeneration contract service or may be performed with onsite regeneration furnace facilities. Large carbon usages (approximately 2,000 lb/day) are required to economically justify onsite regeneration facilities.

Powdered Activated Carbon With Activated Sludge

One of the most promising applications of PAC is in the activated sludge process. The PAC with activated sludge process is a recently developed modification to the activated sludge process that has been demonstrated to significantly upgrade the effluent quality of the conventional activated sludge treatment system. In this process, powdered activated carbon is added to the activated sludge aeration basin thus enhancing the organic removal through adsorption and also by some interaction with the biological system. Compared to other tertiary treatment processes, PAC with activated sludge may have considerable economic advantages. The primary economic advantage is the low capital expenditure required to convert an existing activated sludge treatment plant to a PAC with an activated sludge treatment process. However, operating costs may be high depending on the desired effluent quality and the required carbon dosage. Although carbon regeneration for the PAC with activated sludge process has been demonstrated to be technically feasible, it may be several years before regeneration equipment develops to the point of making regeneration economically attractive.

A typical treatment scheme utilizing a PAC treatment process is shown in Figure 3. The aeration basin should have sufficient mixing to maintain the carbon and mixed liquor in suspension. The solids loading on the secondary clarifier is increased because of the additional carbon in the mixed liquor; therefore, coagulant usage may be required to enhance solids settling and, hence, prevent overloading the

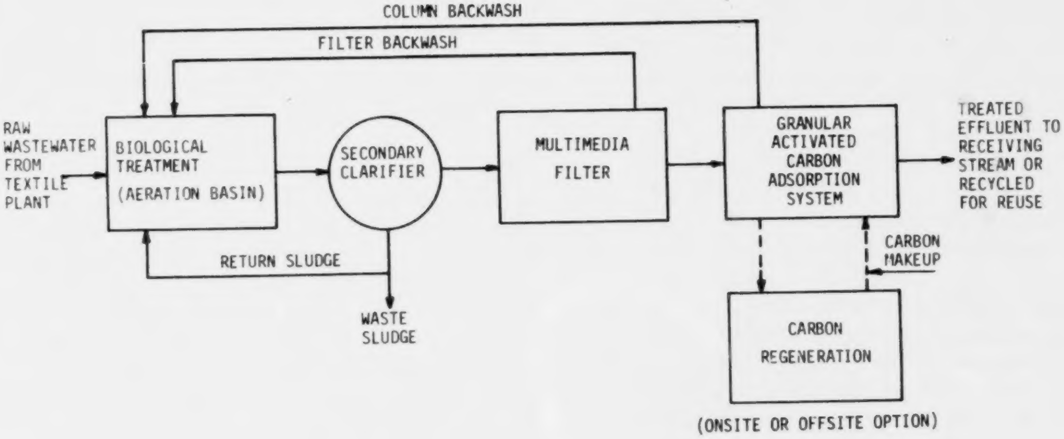

COLUMN BACKWASH
FILTER BACKWASH
RAW WASTEWATER FROM TEXTILE PLANT
BIOLOGICAL TREATMENT (AERATION BASIN)
SECONDARY CLARIFIER
MULTIMEDIA FILTER
GRANULAR ACTIVATED CARBON ADSORPTION SYSTEM
TREATED EFFLUENT TO RECEIVING STREAM OR RECYCLED FOR REUSE
RETURN SLUDGE
WASTE SLUDGE
CARBON MAKEUP
CARBON REGENERATION
(ONSITE OR OFFSITE OPTION)

Figure 1. Typical wastewater treatment scheme utilizing a GAC tertiary system.

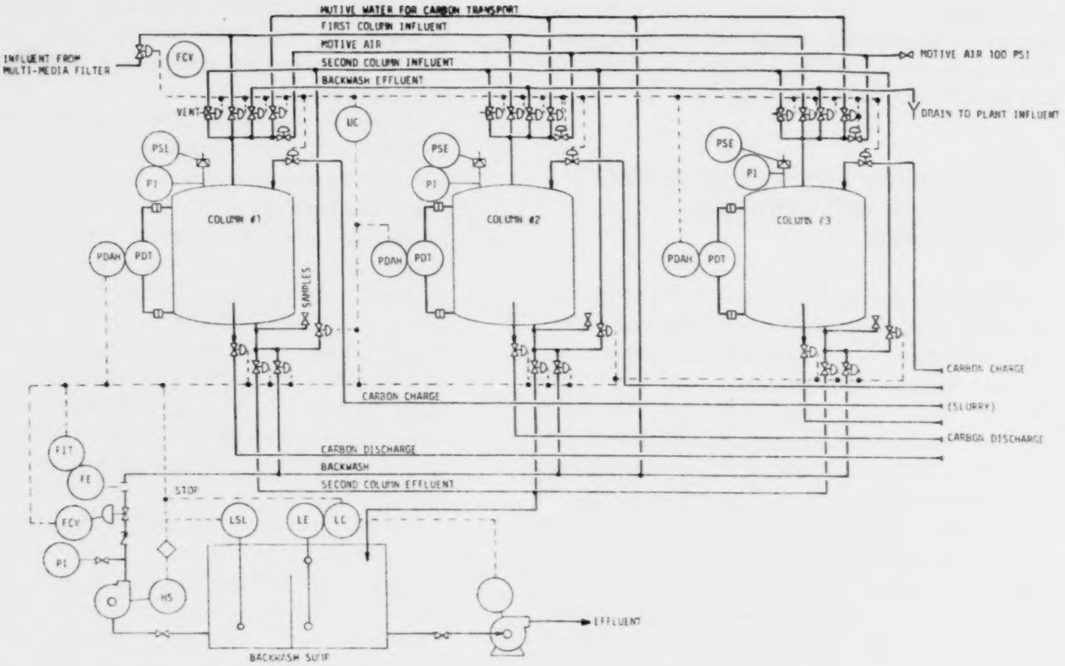

MOTIVE WATER FOR CARBON TRANSPORT
FIRST COLUMN INFLUENT
MOTIVE AIR
SECOND COLUMN INFLUENT
BACKWASH EFFLUENT
INFLUENT FROM MULTI-MEDIA FILTER
FCV
MOTIVE AIR 100 PSI
VENT
DRAIN TO PLANT INFLUENT
UC
PSL
PSE
PI
COLUMN #1
COLUMN #2
COLUMN #3
PDAH
PDT
SAMPLES
CARBON CHARGE
(SLURRY)
CARBON DISCHARGE
BACKWASH
SECOND COLUMN EFFLUENT
FIT
FE
STOP
LSL
LE
LC
HS
EFFLUENT
BACKWASH SUMP

Figure 2. Conceptual process flow diagram activated carbon adsorption.

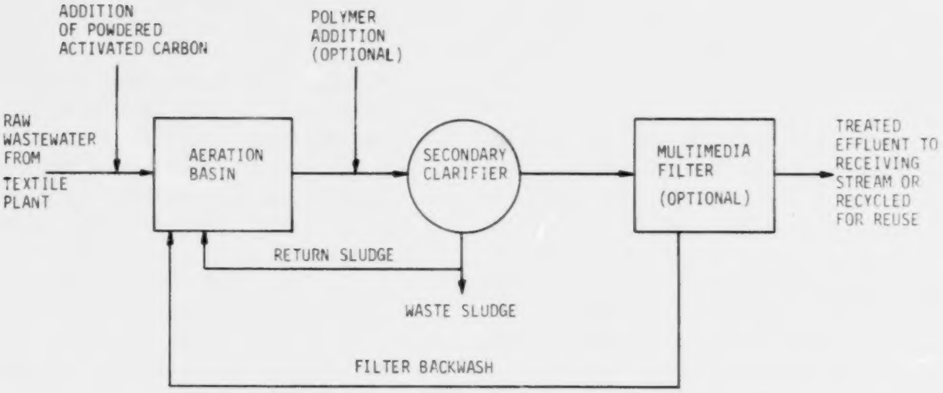

ADDITION OF POWDERED ACTIVATED CARBON
POLYMER ADDITION (OPTIONAL)
RAW WASTEWATER FROM TEXTILE PLANT
AERATION BASIN
SECONDARY CLARIFIER
MULTIMEDIA FILTER (OPTIONAL)
TREATED EFFLUENT TO RECEIVING STREAM OR RECYCLED FOR REUSE
RETURN SLUDGE
WASTE SLUDGE
FILTER BACKWASH

Figure 3. Typical wastewater treatment scheme utilizing a PAC with activated sludge treatment process.

secondary clarifier. Powdered activated carbon added to the mixed liquor means more waste sludge is produced for disposal. However, the powdered carbon may improve dewatering characteristics of the sludge although sometimes the reverse has been shown to be true. The addition of multimedia filtration after secondary clarification is an option that is dependent on the desired effluent total suspended solids level.

PAC has also been applied with limited success on a tertiary treatment process either in a single-stage rapid mix-clarification step, as in a reactor clarifier, or in a multistage countercurrent application. This approach has not been proven economically competitive with GAC due to poorer inherent adsorption efficiency and problems in regeneration.

EXPERIMENTAL TESTING OF CARBON ADSORPTION WITH TEXTILE WASTEWATER

Extensive indepth carbon adsorption experimental studies have been conducted over the last 2 years with textile wastewaters in a project jointly sponsored by the American Textile Manufacturers Institute, Northern Textile Association, Carpet and Rug Institute, and the U.S. Environmental Protection Agency. As part of this project, GAC was evaluated for tertiary treatment with pilot-scale equipment at 19 textile plants that were chosen as representatives of the various subcategories in the industry. The PAC with activated sludge process was also evaluated with bench-scale equipment using wastewaters from 10 representative textile plants. The results from these studies indicate potential effectiveness of carbon adsorption for textile wastewater treatment.

Granular Activated Carbon Experimental Studies

The GAC tests were conducted in two mobile pilot plant trailers that were transported to the 19 textile plant sites during a 17-month period from May 1977 to September 1978. Effluents from the existing biological treatment plants were used as influents to the pilot plant units. Hence, variability of best practical treatment (BPT) plant effluent quality was incorporated into the technical evaluation of pilot-scale performance.

The GAC pilot equipment consisted of a multimedia filter unit followed by three carbon columns operated in series. A sketch of the filter unit is presented in Figure 4. The flow rate to the 13.5-in. diameter pilot filter was varied between 1 and 7 gpm, which represented a surface loading rate of 1 to 7 gpm/ft^2. The optimum surface loading rate for the filter (based on head loss, effluent quality, and filter run time) was determined during an initial 2- to 3-week screening period at each plant site. The filter was operated at a selected optimum rate (if secondary effluent characteristics remained relatively constant) during the remainder of the experiment at that site.

A sketch of a single carbon column is shown in Figure 5. The carbon selected for the individual experiments was based on a preliminary comparison of TOC and color adsorption isotherms for each wastewater with both a lignite- and bituminous-based carbon. Three pilot carbon columns were operated in series with an empty-bed retention time of 45 minutes (total) unless individual wastewater characteristics dictated a longer or shorter retention time. Samples were collected before and after each column in order to monitor breakthrough and exhaustion by developing breakthrough curves. Single-cycle carbon regeneration tests were performed on the spent carbon samples from 12 different sites.

The COD reduction performance with the GAC pilot units is summarized by a bar chart in Figure 6. COD is one of seven promulgated effluent guideline parameters and it is the parameter that can generally be effectively reduced with carbon adsorption. The GAC process obtained the highest percent COD reduction in Subcategories II (Wool Finishing), V (Knit Finishing), and VI (Carpet). The GAC process was not as effective for overall percentage COD reductions in Subcategories I (Wool Scouring), IV (Woven Fabric Finishing), and VII (Stock and Yarn Dyeing). With the addition of the GAC process for tertiary treatment it can be predicted that the presently promulgated best available technology economically achievable (BATEA) guideline limitations for conventional pollutants can be achieved on a technical basis in Subcategories I, II, V, and VI, but could not be achieved in Subcategories IV and VII. This does not mean that the GAC process is the most cost-effective treatment alternative, indeed there may be other less expensive processes that are suitable, only that it is technically feasible in the Subcategories mentioned above (I, II, V, and VI). The economic effectiveness and economic impacts of the application of these technologies is still under review by participating organizations.

The results from the carbon regeneration

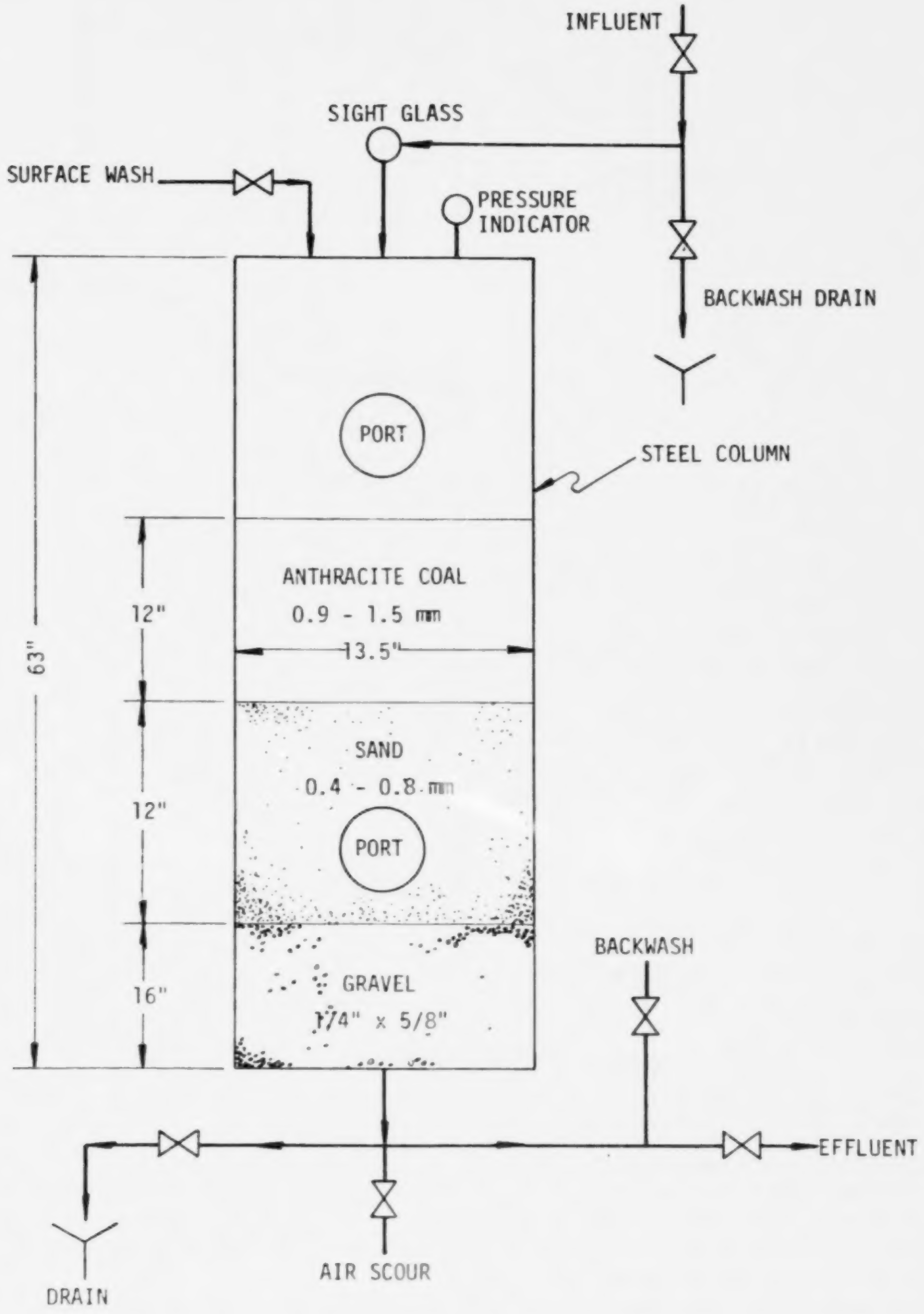

INFLUENT
SIGHT GLASS
SURFACE WASH
PRESSURE INDICATOR
BACKWASH DRAIN
PORT
STEEL COLUMN
ANTHRACITE COAL
0.9 - 1.5 mm
13.5"
12"
63"
SAND
0.4 - 0.8 mm
12"
PORT
BACKWASH
GRAVEL
1/4" x 5/8"
16"
EFFLUENT
DRAIN
AIR SCOUR

Figure 4. Sketch of pilot multimedia filter unit.

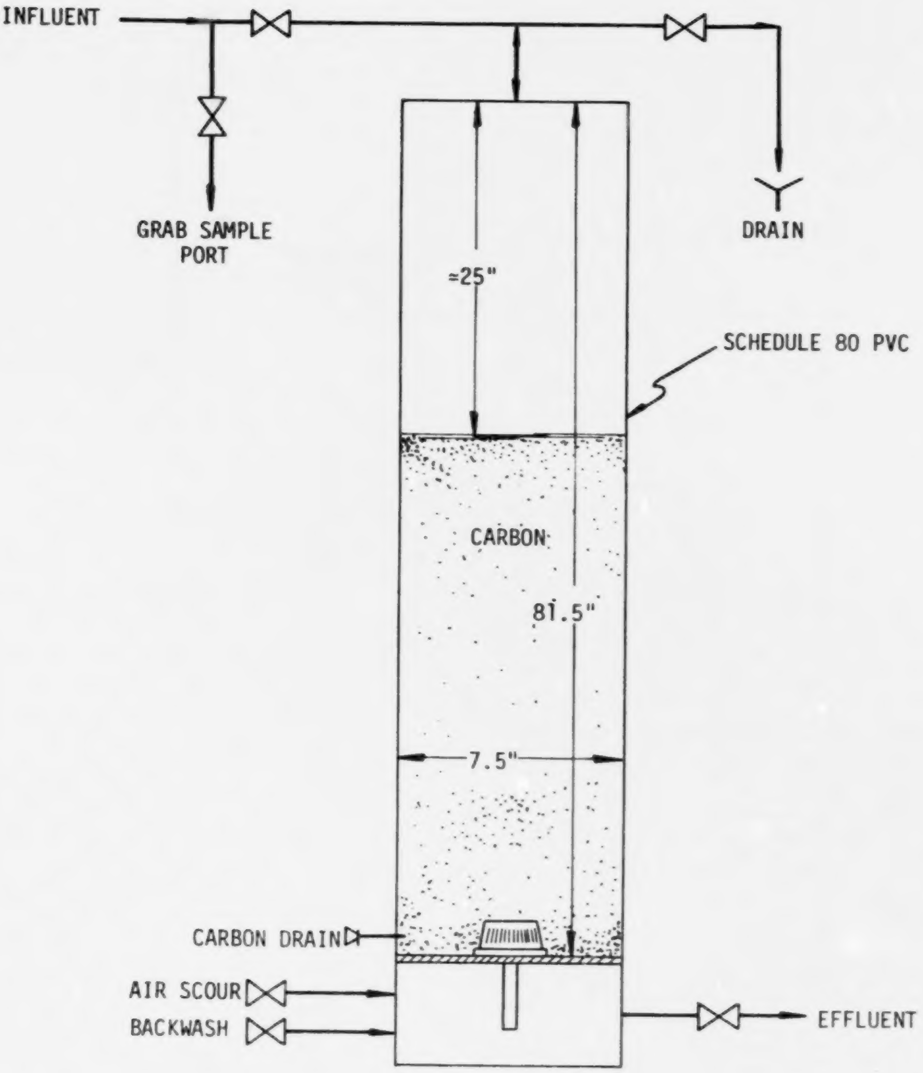

INFLUENT
GRAB SAMPLE PORT
DRAIN
≈25"
SCHEDULE 80 PVC
CARBON
81.5"
7.5"
CARBON DRAIN
AIR SCOUR
BACKWASH
EFFLUENT

Figure 5. Sketch of pilot carbon column unit.

tests, after one adsorption-regeneration cycle, indicated the carbon was successfully regenerated in all cases. No unusual or major problems are indicated in regenerating the granular carbon, based on this preliminary data.

Wastewaters from Subcategory IV (Woven Fabric Finishing) and Subcategory VII (Stock and Yarn Dyeing) were not particularly amenable to carbon adsorption for COD removal. Throughout both subcategories, problems related to nonadsorbability of certain COD fractions as well as COD "stripping" were observed. Identification of specific compounds and wastewater characteristics contributing to this effect demands further detailed study.

Powdered Activated Carbon With Activated Sludge Experimental Studies

The PAC with activated sludge experiments were conducted on a bench-scale basis as a preliminary screening evaluation to determine the

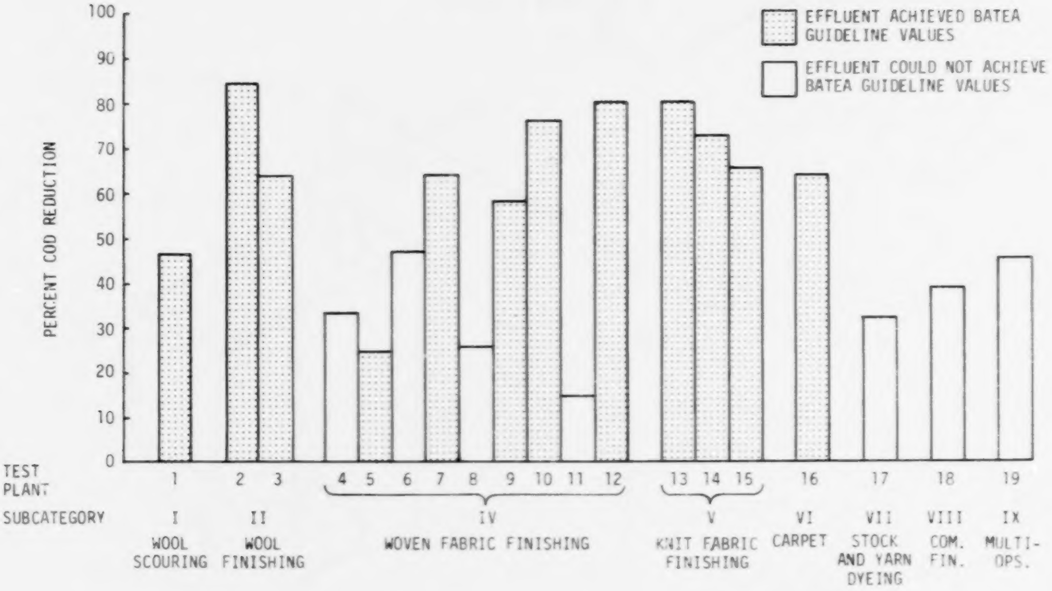


Figure 6. Summary of COD reduction performance with GAS pilot units.

technical feasibility of the process as applied to textile wastewaters. Ten textile plants representing the various subcategories were selected for the study. Raw waste samples were shipped weekly to the Engineering Science, Inc. laboratory in Atlanta, Georgia during the study period. Several different test conditions, primarily with regards to carbon dosage, were evaluated simultaneously in the lab.

Each plant experiment was conducted utilizing three 10-liter plexiglas bioreactors (similar to the one shown in Figure 7). The three bioreactors were seeded with activated sludges from the textile mill and a municipal/industrial wastewater treatment plant and subsequently acclimated to the textile wastewater. After acclimation was achieved, TOC isotherms were performed on the bioreactor effluent to select a powdered carbon (lignite or bituminous base) and carbon dosage range to evaluate. The carbon dosages were typically in the range of 1,000 to 10,000 mg/liter (in the mixed liquor) in order to bracket the expected technically effective range. Carbon was added at the selected high and low carbon dosages to two of the bioreactors and the system was allowed further time to acclimate. The third bioreactor was operated as a control unit. Data was collected and evaluated after steady-state was achieved in the three bioreactors.

The results of the PAC with activated sludge screening tests with the ten textile plant wastewaters are summarized in the bar charts in Figure 8. The PAC with activated sludge treatment process was generally successful in improving the effluent quality in bench-scale evaluations of wastes from Subcategories II, IV, V, VI, and VII, but was not effective with waste from Subcategory I. The treatment effectiveness in Subcategory I (Wool Scouring) was probably reduced by the higher oil and grease levels in the raw wastewater. Based on the favorable results from the screening studies, a second level of onsite pilot-scale testing at selected plants from Subcategories IV and V has been recommended.

SUMMARY

Recent studies have been completed evaluating carbon adsorption technology for advanced waste treatment of textile wastewaters. Granular carbon adsorption pilot tests were conducted with secondary effluents from

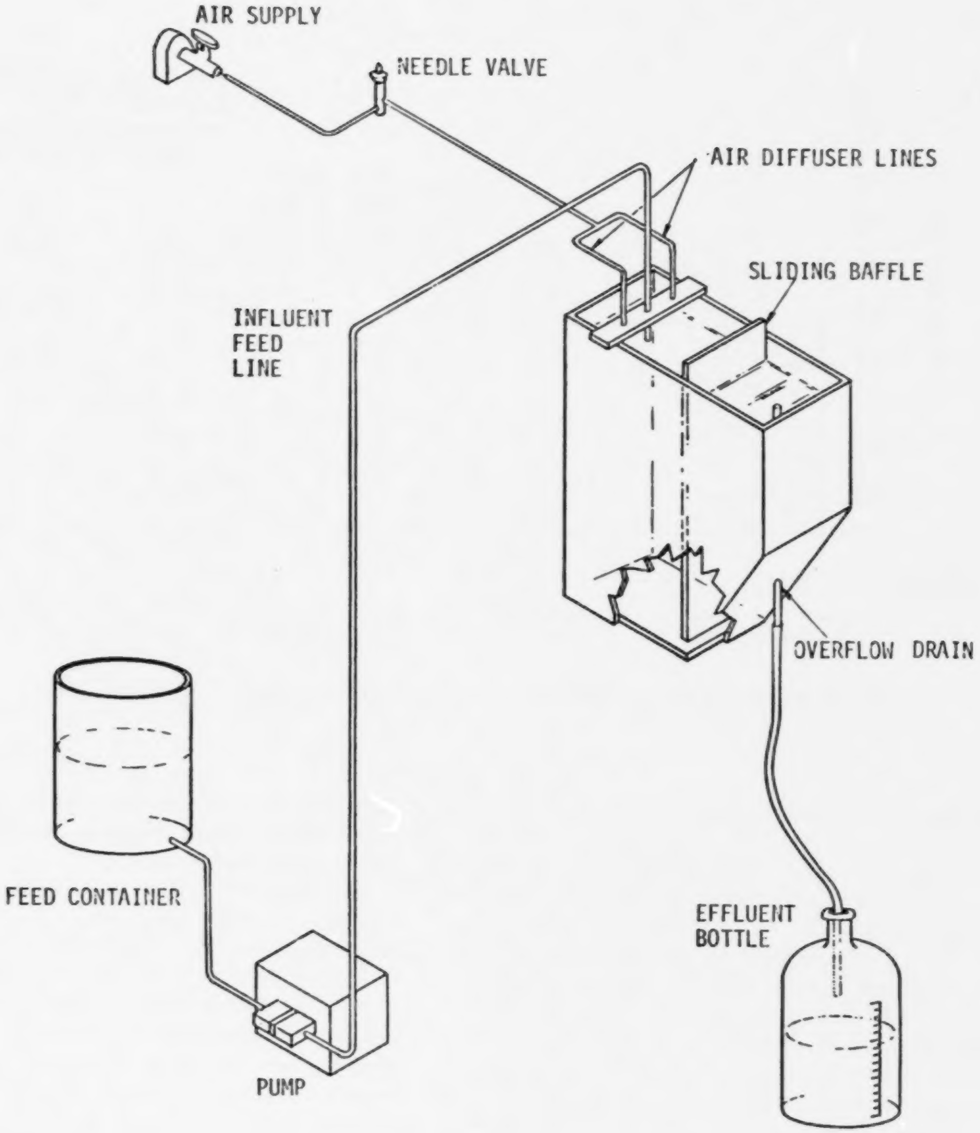

AIR SUPPLY
NEEDLE VALVE
AIR DIFFUSER LINES
SLIDING BAFFLE
INFLUENT FEED LINE
OVERFLOW DRAIN
FEED CONTAINER
EFFLUENT BOTTLE
PUMP

Figure 7. Experimental biological reactor.

19 representative textile wastewaters. Granular carbon adsorption pilot tests were conducted with secondary effluents from 19 representative textile plants, and bench-scale powdered activated carbon with activated sludge screening tests were conducted with ten textile wastewaters. The following observations were developed from evaluating these experimental studies.

- The granular activated carbon pilot studies demonstrated reasonable effectiveness for reducing secondary effluent COD concentrations (63 to 84 percent) of textile plants in Subcategories II, V, and VI, but only marginal COD removal effectiveness (14 to 80 percent) was achieved in Subcategories I, IV, and VII.
- From the results of the granular activated

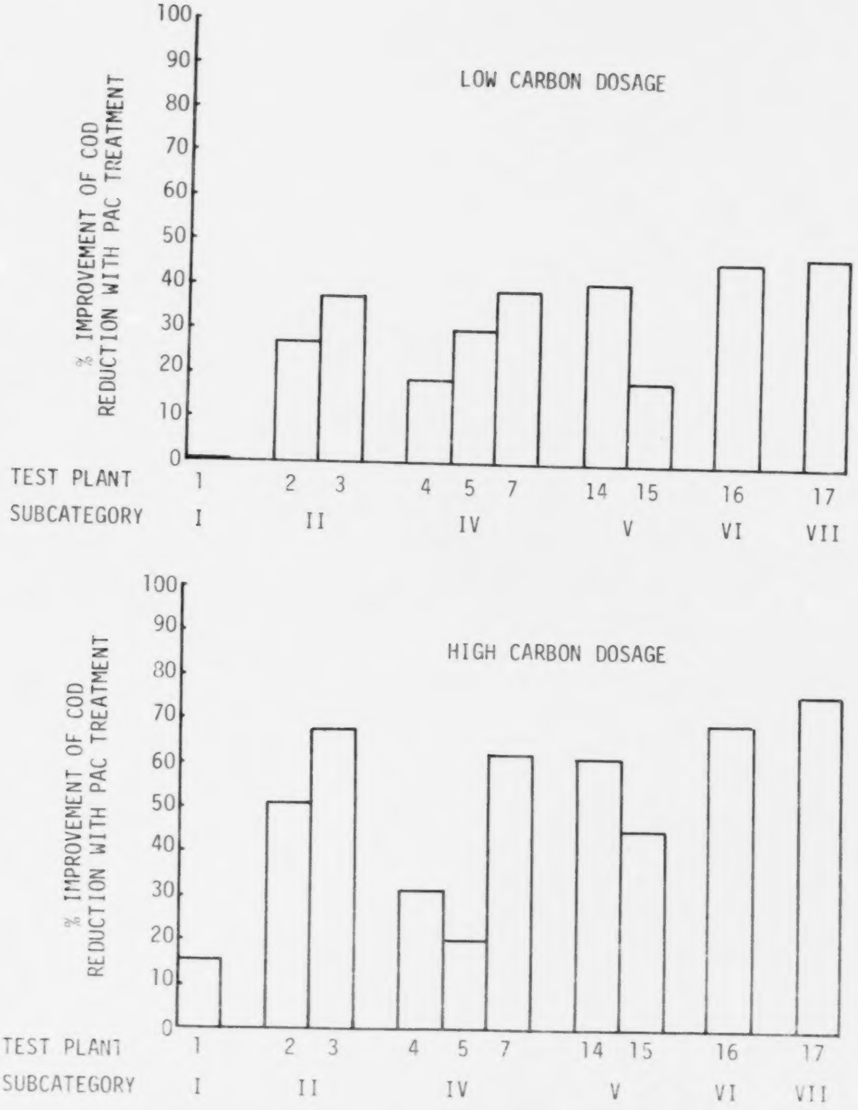


Figure 8. Summary of COD reduction performance from bench-scale PAC with activated sludge treatment.

carbon pilot studies, it can be predicted that the presently promulgated BATEA effluent guideline values could be technically achieved with a granular activated carbon tertiary treatment process in Textile Subcategories I, II, V, and VI, but not in Subcategories IV and VII. This does not mean that the granular activated carbon process is "economically achievable" or that it is more cost-effective than other advanced waste treatment processes.

- The bench-scale screening tests evaluating powdered activated carbon with activated sludge indicated that improvement in COD removal performance (19 to 69 percent) could be achieved in all Textile Subcategory plants tested except Subcategory I.

BIOLOGICAL TREATMENT OF TEXTILE WASTE BY AERATION

T. A. Alspaugh, John Hodges, Arthur Toompas*

Abstract

Biological treatment systems have shown the adaptability and flexibility to handle almost any textile waste mixture. This blending of prehandling, treatment, waste characteristics, and effluent results, necessary with space requirements and operation costs, has produced the numerous textile wastes treatment systems found in the industry. These systems have been shown to handle shock loads and vary wastes characteristics, while producing good results at a reasonable construction and operating cost.

INTRODUCTION

The words "textile wastes" mean the wastewater from the manufacturing and processing of textile fibers or fabrics containing natural and/or synthetic fibers. In more specific terms lint, trash, grease, and other residue from fiber cleaning; wastes from the manufacturing or greige operations, including size material; the wastes from desizing, scouring, bleaching, and mercerizing before dyeing and finishing; all dye bath dumps, overflows, and rinses; finish bath dumps, overflows, and rinses; machine and equipment spills, cleanups, and the like. The mixture will be warm with the temperature depending on the use of heat exchangers. The chemical content will depend upon the type fiber, fibers, or fabric processed.

The natural fibers usually encountered in the United States are wool and cotton. Wastewater from wool preparation will be very strong, high in grease, BOD, COD, total suspended solids (TSS), heavy metals, and color, but usually low in pH. The contaminant material removed from wool by scouring is the major problem. Wool finishing wastes will be much weaker in all aspects with a near neutral pH. Cotton, on the other hand, produces a wastewater high in pH due to caustic use in mercerizing and/or cleaning the fibers. The BOD will be moderate, the TSS usually on the low side with trace heavy metals and with varied color, but high COD coming from the processing chemicals. Synthetic fiber process wastewater will be near neutral in pH, low in TSS, moderate BOD and COD and, with a weak color. The major problems are the materials used to aid the dye in penetrating and staying on the fibers.

A total mixture then can have a low to high pH depending on the processed fiber, will be colored, and can contain grease, fibers, lint, and trash from the fiber. The mixture will contain processing chemical residues, size, penetrants, wetting agents, detergents, carriers, dyes, finishes, etc., all mixed in the water used in processing to rinse or wash the fabric or fiber, to dye it, and to finish it. (Tables 1, 2, and 3)

TABLE 1. RAW WASTES ANALYSIS – BLEND OR COTTON

pH	10-12
BOD, mg/l	600-1,000
COD, mg/l	1,000-2,000
TSS, mg/l	70-100
Color	Varied (dark)
Cr, mg/l	0-0.50
Zn, mg/l	0-1.0
TKN, mg/l	10-20
TPO_4, mg/l	10-15

METHODS OF BIOLOGICAL TREATMENT

There are a number of treatment alternates available for the biological treatment of textile wastes. Based on work carried out within the industry, any of these waste mixtures can be treated satisfactorily either by aeration systems or biological filters if the necessary prehandling is done. This prehandling involves

---

*Chemical Engineer, Engineering Department, Cone Mills Corporation, Greensboro, NC.

Preceding page blank

pH adjustment in some cases and the addition of nutrients (nitrogen and/or phosphorus). In others, possible removal of lint, grease, or trash, equalization if needed, and removal or replacement of processing chemicals when toxic to the biological treatment process.

Except for oxidization ponds, most of the different aeration type biological systems for treatment of textile wastes can be found listed in the Metcalf & Eddy, Inc. book entitled *Wastewater Engineering: Collection, Treatment, Disposal* under the heading "The Activated Sludge Process." These include conventional, complete-mix, step-aeration, modified-aeration, contact stabilization, extended-aeration, Kraus process, high-rate aeration, and pure oxygen systems.

TABLE 2. RAW WASTES ANALYSIS – SYNTHETIC

pH	6-9
BOD, mg/l	200-400
COD, mg/l	400-800
TSS, mg/l	40-80
Color	Varied (lighter)
Cr, mg/l	0-0.3
Zn, mg/l	0-1.0
TKN, mg/l	5-15
TPO_4, mg/l	5-10

TABLE 3. MIXED WOOL WASTE

	Scouring	Finishing
pH	2-5	5-7
BOD, mg/l	2,300	180
COD, mg/l	6,000	740
TSS, mg/l	2,500	200
Cr, mg/l	—	0.6
Zn, mg/l	—	—
PO_4, mg/l	—	—
TKN, mg/l, mg/l	—	—
Phenol	—	.04

The information included in Table 4 indicates the various systems that have been used for textile waste treatment. (Figures 1 through 9)

Aerobic biological treatment sounds simple enough but has required extensive laboratory, pilot work, and full-scale systems to convince regulatory agencies that it would work, and was both feasible and practical. This early work developed the minimum maintenance, long aeration time period activated sludge type waste treatment system generally found throughout the textile industry today. This system uses the aeration time period to buffer the waste, blend it, absorb the shock loads, and allow acclimation of biological organisms to the

TABLE 4. OPERATING CHARACTERISTICS OF WASTE TREATMENT SYSTEMS FOR TEXTILES

	Detention period	Flow model	Recycle	Aeration type	BOD removal efficiency %	Application
Trickling filter	10-20 min	Plug	1/1 to 4/1	NA	50-85	Susceptible to shock loads; used for weak strength textile wastes, mixed domestic sewage, and textile wastes
Bio-disc	Depends on tank size	Completely mixed	.3/1 to 1/1	NA	85-95	Useful for plant expansions, medium strength textile wastes, in combination with activated sludge for strong wastes
Oxidization ponds	5-50 days	Plug flow	0-1/1	Wind currents or mech. aerators	60-85	Weak strength textile wastes, susceptible to shock loads
Conventional AS	6-8 h	Plug flow	.3/1 to 1/1	Diffused air, mech. aerators	80-90	Susceptible to shock loads, weaker textile wastes, and/or domestic wastes (not used frequently)
Completely mixed AS	24-48 h	Completely mixed	1/1 to 3/1	Diffused air, mech. aerators	85-99	General application, resistant to shock loads
Step aeration	6-8 h	Plug flow	.3/1 to 1/1	Diffused air	70-85	General application (not used frequently)
Contact stabilization	1-h contact 3-8 stab.	Plug flow	.3/1 to 1/1	Diffused air, mech. aerators	80-90	Flexible; useful for plant expansions,small to medium plant, package plants (not used frequently)
Extended aeration	24-120 h	Completely mixed	1/1 to 3/1	Diffused air, mech. aerators	75-95	Variable strength wastes, small and medium sized plants
Oxygen/activated sludge	8-24 h	Completely mixed	.3/1 to 1/1	Mechanical aerators	85-95	General application on all textile wastes, use where land space is limited

Source: Reference 1.

material. The method and/or methods used depends on the type and strength of the waste, land availability, power cost, labor cost, efficiency required, etc. In general, the processes used for textile wastes treatment have tended to fall into the completely mixed or extended aeration category or a hybrid of these two, with some scattered biological filter systems.

Completely mixed systems are most often used for strong, highly colored wastes, usually with detention aeration periods of from 24 to 48 hours. They tend to carry higher mixed liquor suspended solids (MLSS) than the other systems and usually require sludge disposal. They most often use mechanical aeration but if not too large and designed properly they can use diffused air. Extended aeration systems on the other hand can be either completely mixed or plug flow, depending upon the type aeration and raw waste distribution devices. Extended aeration uses low organic loadings and much longer aeration time periods; up to 5 days in some cases to handle the wastes. Since the space required to treat a large volume with high or moderate organic concentrations by this method is large, extended aeration is most often used for small to medium plants or weaker wastes unless land is available. (ref. 1)

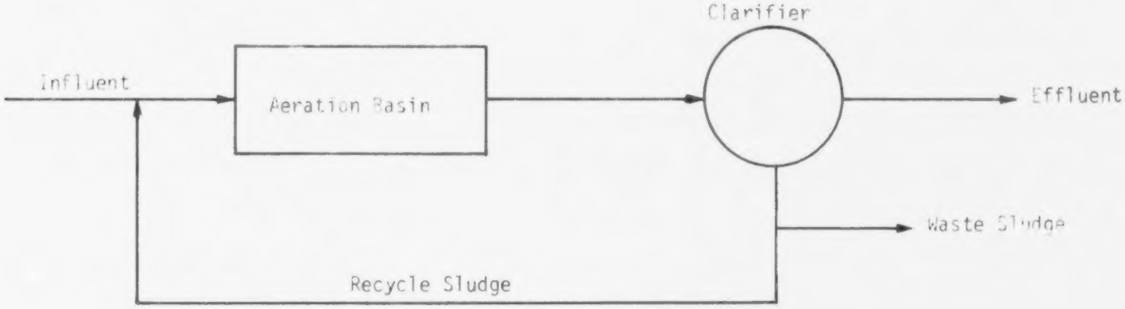

Influent
Aeration Basin
Clarifier
Effluent
Waste Sludge
Recycle Sludge

Figure 1. Conventional activated sludge system.

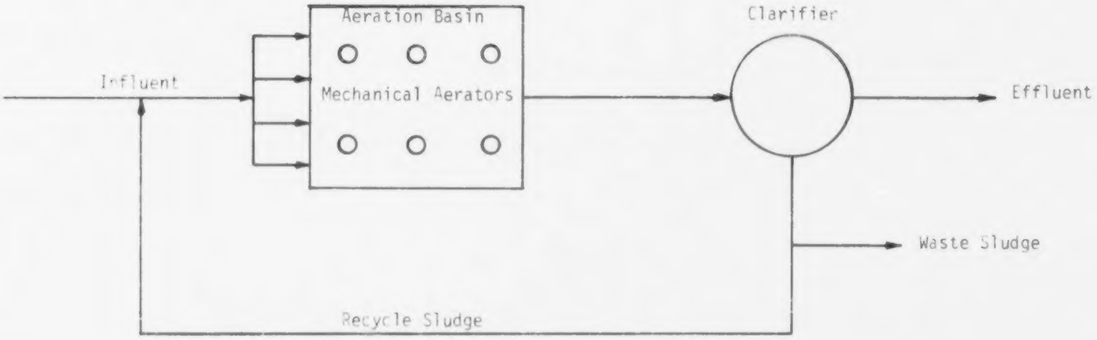

Aeration Basin
Influent
Mechanical Aerators
Clarifier
Effluent
Waste Sludge
Recycle Sludge

Figure 2. Completely mixed activated sludge system.

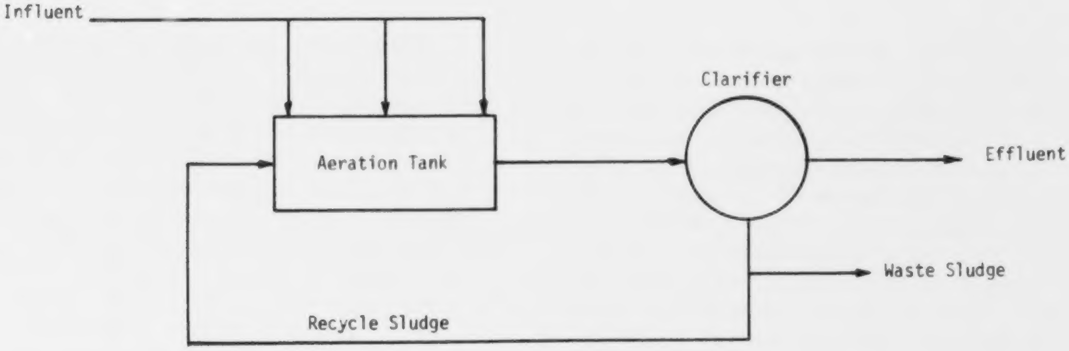

Influent
Clarifier
Aeration Tank
Effluent
Waste Sludge
Recycle Sludge

Figure 3. Step aeration activated sludge system.

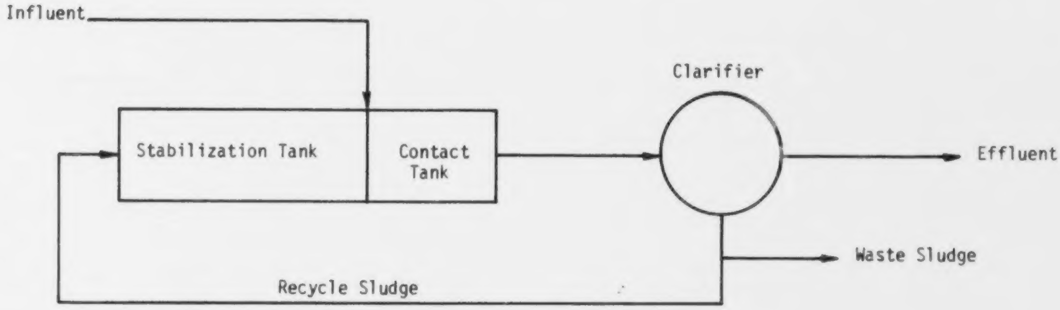

Influent
Clarifier
Stabilization Tank
Contact Tank
Effluent
Waste Sludge
Recycle Sludge

Figure 4. Contact stabilization system.

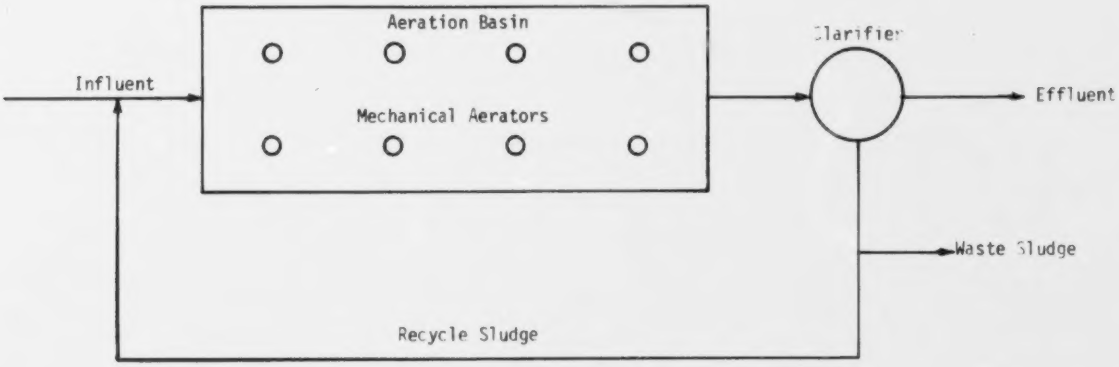

Aeration Basin
Clarifier
Influent
Mechanical Aerators
Effluent
Waste Sludge
Recycle Sludge

Figure 5. Extended aeration activated sludge system.

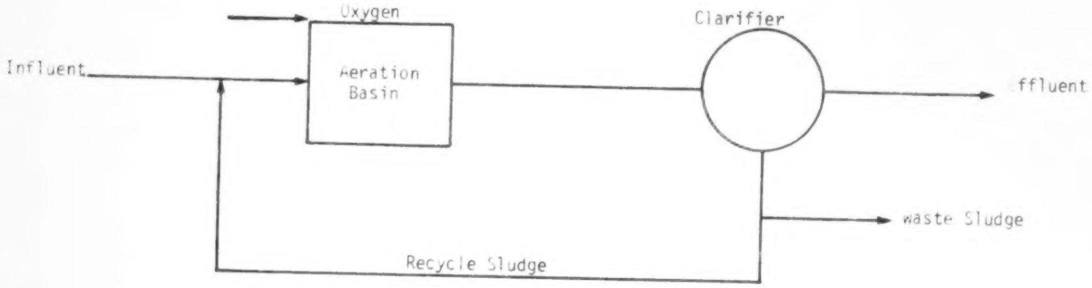

Oxygen
Influent
Aeration Basin
Clarifier
Effluent
Waste Sludge
Recycle Sludge

Figure 6. Oxygen/activated sludge system.

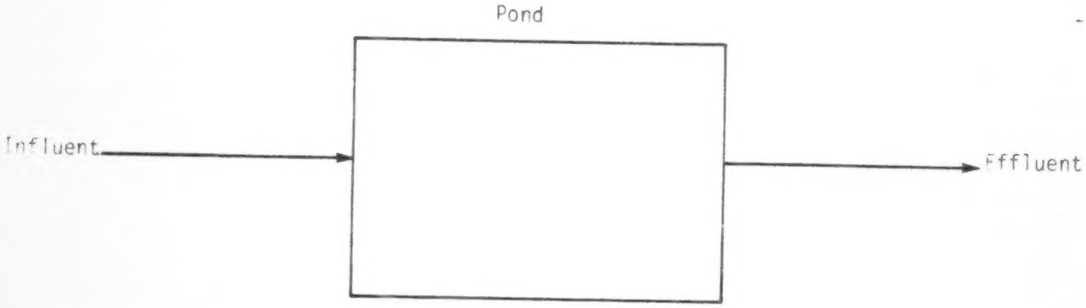

Pond
Influent
Effluent

Figure 7. Oxidation pond system.

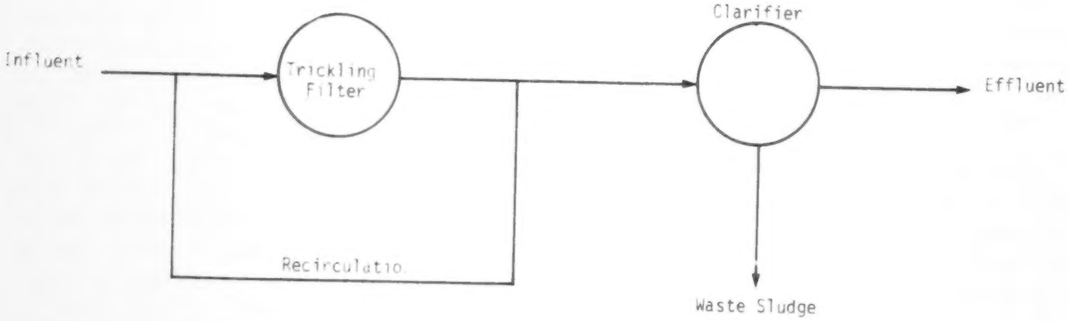

Influent
Trickling Filter
Clarifier
Effluent
Recirculation
Waste Sludge

Figure 8. Trickling filter system.

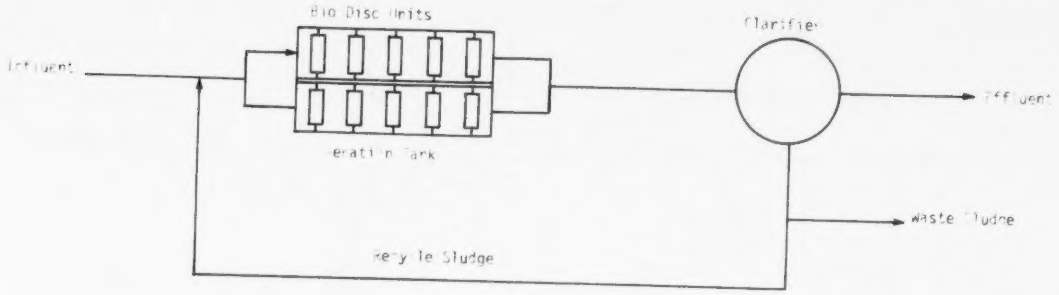


Figure 9. Bio-disc activated sludge system.

Oxidation ponds are shallow lagoons or basins, usually not over 6- to 7-ft deep and even as shallow as 4 ft, and use natural processes to treat the waste with or without the use of mechanical means for mixing or aeration. Solids will settle to the bottom of the lagoon or pond and if so, are decomposed anaerobically. The suspended organic solids are decomposed by aerobic bacteria that use surface aeration. Algae can grow on the surface of lagoons of this sort using the nitrogen and phosphorus in the incoming waste for nourishment. A system of this type can be a dual aerobic/anaerobic system; aerobic on top, anaerobic on the bottom. This type of system has a limited use in particular situations for weak, easily oxidized wastes where land is available and the climate is warm. (ref. 2)

The pure oxygen aeration system is becoming more popular as a means of treating highly concentrated waste. The aeration basin, in general, will be smaller, possibly covered, and contain oxygen mixed with the waste. This process results in a more rapid production of a biological floc, which reportedly has better settling characteristics, and is said to be more efficient than a system using air as its oxygen source. The molecular sieve is one device being used to generate the pure oxygen onsite. As electric power costs increase, oxygen systems are forecast to become more prominent.

The trickling filter is another biological treatment system that has found some use in certain situations. Trickling filters are normally beds of media 5- to 20-ft deep with influent spray distribution systems and underdrain systems for effluent collection. The sprays discharge onto the bed of filter medium which contains the bacteria or other biota. This slime absorbs and breaks down organic matter in the wastewater. The concentration of the influent waste is diluted by recirculating a portion of the filter effluent back to the incoming waste. A major difference between activated sludge and trickling filters is that the trickling filter uses a series of biological communities at various levels in the unit and each series has its own type of life and its own degrees of removal.

Strong waste, however, can cause sloughing off of matter and biomass from the media. Although recirculation is widely practiced and forced air used in some cases, the trickling filter normally lacks the inherent buffering capacity of activated sludge. Waste that is not readily biodegradable will not be removed effectively by trickling filters due to the shorter detention period in contact with the active organisms.

The rotating biological disc is an effort to overcome some of the disadvantages of the biological trickling filter. It is a series of closely spaced perforated discs rotating partially submerged in waste and the dripping, turning disc aerates and mixes the waste and the active organisms. This process tends to overcome the lack of long-term contact inherent with the conventional filter. In some cases rotating discs have been added to activated sludge plants as a means to increase treatment. Many textile plants that have been operating for some period of time can become overloaded as production increases. Rotating discs may be added to upgrade an existing plant as an improvement step and provide a large amount of surface area in a small space for bacteria to attach to and thus increase removal. Bio-discs usually have to be covered as they are affected by air temperatures and cold weather.

Numerous relationships have been developed to explain the actions of the various aerobic biological systems. For activated sludge these relationships may include:

- Waste strength vs. mixed liquor suspended solids concentration,
- Waste strength vs. detention time,
- pH reduction as function of CO_2 production by aeration,
- Color removal vs. mixed liquor suspended solids concentration,
- Organic removal vs. mixed liquor suspended solids concentration,
- Effluent heavy metal concentration vs. sludge concentration,
- Effluent heavy metal concentration vs. sludge removal rate,
- Efficiency of removal vs. aeration detention time,
- Efficiency of removal vs. cost of power, and
- Removal rate as a function of recirculation.

And for biological filters and rotating discs, they may include:

- Removal rate as a function of recirculation,
- Removal rate as a function of media volume or surface area,
- Waste strength vs. detention time (Figure 10),
- Removal rates vs. disc speed, and
- pH reduction vs. recirculation rate.

CONTROL PARAMETERS FOR PLANT DESIGN & OPERATION (Figures 10 and 11)

Food-to-Mass Ratio

The waste loading or food-to-mass (F/M) ratio is used to control the rate of biological activity in an activated sludge system. The F/M ratio is the amount of BOD applied per day

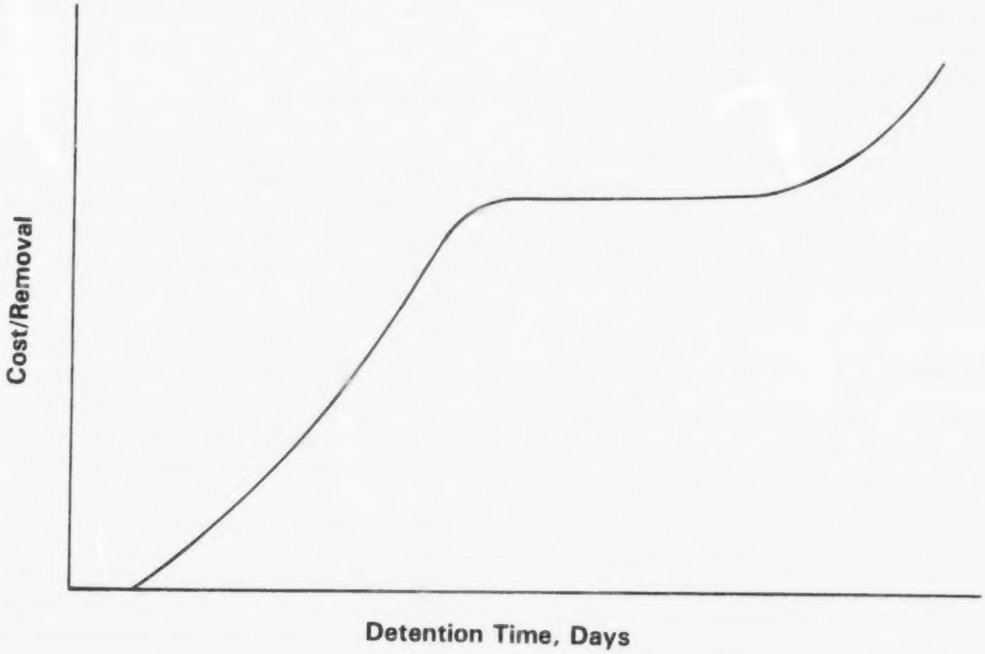


Figure 10. Effect of increased detention time on cost and removal.

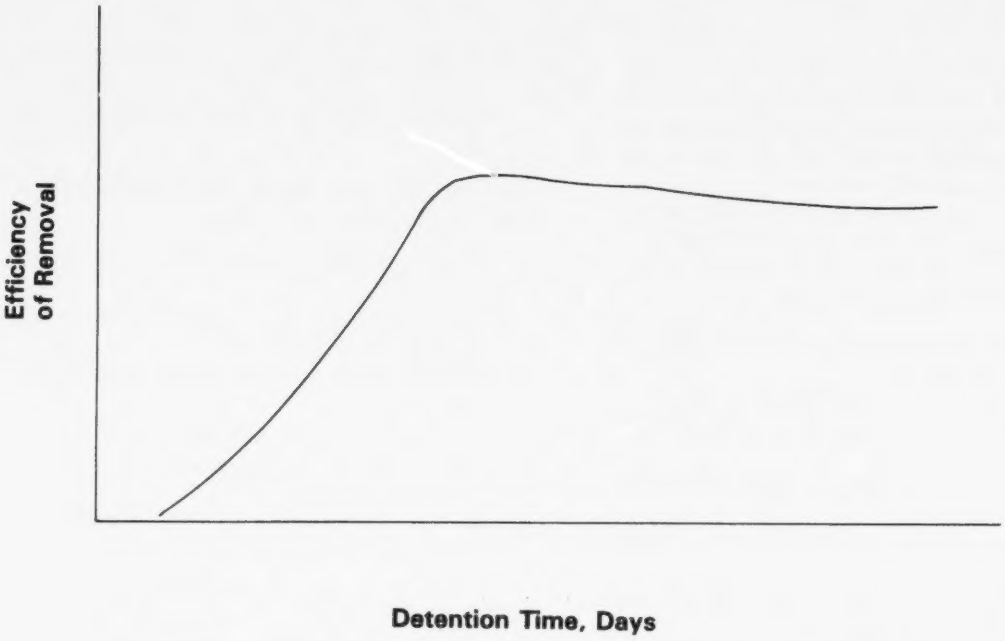


Figure 11. Effect of increased detention time on treatment efficiency.

divided by the amount of volatile suspended solids in the aeration basin. As a general rule, high F/M ratios tend to give better settling solids. However, if F/M ratios are too high, some hard to break down BOD may not be broken down and removal efficiencies may suffer. If low F/M ratios are used, one may expect better organic removal efficiencies, although a poor settling sludge sometimes occurs. In general, textile waste can accept lower F/M loadings than municipal waste (0.05 to 0.15), however, ideal levels should be set on a case-by-case basis.

Recycle Rate

The recycle rate is the volume of liquid returned sludge divided by the incoming volume of wastewater to be treated. This rate can be varied in order to prevent solids from leaving the plant in the effluent. If the return rate is too low then septic solids along with solids in the effluent sometimes can be expected. If the return rate is too high, problems with hydraulic loadings and difficulties in maintaining an adequate sludge blanket can occur. Textile wastes normally require return rates of 100 to 300 percent while municipal waste treatment plants use lower recycle rates.

Solids Level

The solids level refers to the concentration of MLSS in the aeration system. At low levels it is difficult to achieve high removals of some organics and high pH or hard-to-treat wastes often cause problems due to a limited buffering capacity. At high solids levels increased color and COD removal is often found along with some problems in suspended solids removal. Again, the MLSS level can be higher when treating textile waste than municipal waste, levels of 2,500 to 4,000 ppm are typical, but 4,000 to 8,000 are not uncommon.

Sludge Volume Index

The sludge volume index (SVI) utilizes information on sludge volume and dry basis solids to give a useful operating parameter. The SVI is the percent volume of sludge settled in 30 minutes divided by the percent of suspended solids in the aeration basin. The sludge density index is 100 divided by the SVI. This parameter is not too useful in very high MLSS.

Sludge Age

Sludge age is the pounds of TSS in the aeration tank per day per pounds of suspended solids added. Sludge age is intended to be an indicator of the activity of the sludge. When sludge is too old it may be considered inactive and may also concentrate undesirable products such as heavy metals and/or toxicants. Low sludge age operation normally causes a more rapid growth of solids which in turn can require more disposal of solids. Again, very long aeration periods with low production rates of solids can tend automatically to have high sludge ages.

Detention Time

Detention time in an aeration basin or filter is the volume of the basin or filter divided by the daily flow rate. This parameter is extremely difficult to increase once a plant has been built, unless the designer happened to sectionalize the system and build in capacity. Most textile wastes require longer detention times than municipal wastes. Aeration basins with 1 to 3 days detention are typical.

METHODS OF PROVIDING OXYGEN

There exist two primary means of aeration to provide oxygen. One is mechanical aeration which includes floating or fixed surface aerators, biological filters, and rotating discs, and the other is diffused air. Mechanical aeration throws the liquid waste up into the air, drips it, or waterfalls it, producing more surface area and allowing more oxygen to be absorbed. Diffused aeration, on the other hand, is inducing compressed air into the waste through air diffusers usually at the bottom of the tank for complete mixing and absorption. There are also some hybrid devices including mixers with diffused air, and air ejectors or jets.

Diffused aeration is usually considered the more expensive method of the two, as the capital costs of installation are larger. It is also considered the more efficient aeration method as most of the horsepower goes to maintain the dissolved oxygen level and less of it goes to strictly mixing. It is most often used in deep basins with vertical walls, normally longer than wide due to the air pattern, and constructed of concrete. Maintenance costs for operation of diffusers in textile waste can be a real problem because they are so subject to plugging.

Surface aerators are of two types: slow speed and high speed and are usually more flexible and easier to maintain than diffused air because individual units can be cut off or removed from the aeration basin without shutting down the system and causing a defficiency in dissolved oxygen. They do, however, transfer somewhat less oxygen per horsepower and often use more horsepower for mixing than aeration. This is due, in the main, to the type of installations in ponds and lagoons. Large shallow ponds and lagoons have a very large surface area when compared to vertical wall concrete basins. In colder climates aerators tend to cool the waste thus slowing down biological activity; diffused air would do the opposite.

Slow speed fixed surface aerators require the construction of a bridge structure and use a speed reduction gear unit. They are less flexible than floating units because the water or waste level cannot be varied to any extent and the individual units are stationary. Maintenance and capital costs tend to be high when compared to a high speed surface unit because of the cost of the speed reduction gear unit and the support platform. Slow speed units are said to have the advantage over high speed units when it comes to floc breakdown. High speed units are said to shear the biological material and to produce a less easily settled floc.

Floating surface aerators require little in the way of structural supports and produce a very flexible aeration system as they can be moved around and are not affected by water level changes. There are again two types: slow speed and high speed. The slow speed unit is just a fixed surface aerator on floats and has most of the same advantages and disadvantages of the fixed unit. The high speed (direct drive) floating surface aerator is the most flexible system of all. It is easy to maintain, but not quite as efficient as either the slow speed mechanical aerator or diffused air. It is, however, usually the least expensive aeration/pound of air delivered if all costs are taken into consideration.

Trickling filters are not used as often on textile wastes as the other methods but can work well on some wastes. The construction costs will be high, but operation costs can be lower unless a mechanical means is used to increase air supply through the unit (fans). They are also subject to weather, especially if above ground in cold climates. Freezing problems can also be encountered with the rotating element during cold weather.

Rotating discs or rotating biological discs are a combination of a biological filter and an activated sludge system and are a successful treatment device. As the cost of power increases, they will become more competitive and their initial cost will possibly overcome the flexibility and ease of handling of the floating high speed (direct drive) surface aerator.

SOLIDS SEPARATION

In order to operate an activated sludge type treatment system efficiently, an optimum biological population must be maintained in the aeration system by settling the solids and returning them to the aeration portion. This settling takes place in clarifiers. The settled sludge is collected by any one of a number of drawoff systems and is picked up by the return sludge pumps for recycling. As discussed previously, the return sludge rate can be a critical factor in the successful operation of this system on textile wastes.

The biological floc from textile waste treatment is often difficult to settle and light sludge is one of the most common problems. This problem can be partially controlled by making sure that the control parameters used and discussed previously are properly regulated; the most effective F/M ratio, sludge age, and sludge concentration must be maintained. Normally if these conditions are met a fairly good settling sludge will result. However, the floc may still tend to be very small and extremely light. Sludge bulking can also be a problem. Since the incoming wastes often are strong and not always consistent, a change in the plant process, if not controlled, can cause temporary rises and falls of highly concentrated waste flows that may upset the system temporarily killing off bacteria that can cause bulking sludge. The growth of filamentous bacteria or a change in water temperature both may also cause bulking or floating sludge. Floating sludge, caused by a change in temperature, is often noted when the air temperature changes rapidly for several days from high to low or low to high in relationship to the water temperature. Bulking from filamentous sludge is more noticeable in cold weather with rapid withdrawal clarifiers, long aeration detention times, and in waste with high carbohydrate fractions.

To reduce the solids content in the clarifier effluent resulting from the carryover of these small fines or when bulking occurs, a weighting agent can be used to aid the settling. A number of organic polymers can be used to coagulate the fine floc and produce a larger, heavier one. Inorganic coagulants such as alum and ferric chloride may also be used. If organic polymers are added they will be oxidized and neutralized when returned to the aeration system, thus a constant feed must be maintained. Inorganic coagulants, on the other hand tend to be recycled. If the use is large and sludge wasting is low, they will in time concentrate in the system and can cause problems themselves. They may reduce the biological activity and result in poor treatment and/or bulking. Powdered and granular activated carbon have also been added to biological treatment plants to aid the biological process and increase settling by weighting the sludge.

Sludge disposal is required for solids that are no longer needed in the system; these solids may contain refractories, nonbiodegradable produced solids, and trace heavy metals. Sludge wasting is determined by the desired F/M ratio, solids level, sludge age, and treatment expected.

Biological treatment sludge has a structure that enables it to absorb color bodies, organic materials, and trace heavy metals. This serves to concentrate these materials and allows them to be removed from the liquid phase in a form that can be concentrated for disposal. Continuous in-plant efforts can serve to remove or replace many of these substances that will end up in this sludge. Chromium use for dye oxidization has been successfully replaced at a higher cost. Zinc, which is everywhere, including the raw water, can be reduced by replacement as a corrosion inhibitor, chemical type changes, replacement by piping, etc.; but many dyes are made with zinc. Other products containing heavy metals that are determined to be hazardous must be replaced or removed. At this time, little long-term data on textile wastes is available to determine levels to be expected or required on other problem heavy metals. The few analyses made to date in textiles indicate that few, if any, other heavy metals will be a problem.

Biological activity and thus sludge production will vary and can be related to F/M ratio. Generally at high F/M ratios (0.15 to 0.20) productivity of sludge is high and is reduced at lower F/M ratios (less than 0.10). However, better settling solids can usually be expected at these higher loading rates, thereby reducing effluent suspended solids and clarifier size. Solids level and sludge age also affect treatment expected, with higher MLSS levels generally giving better color and COD removals, however, high effluent suspended solids may be expected at these high solids levels. Very long aeration detention times also can result in poorly settling sludge. This can often be handled with larger clarifiers and lower overflow rates. Nutrient removal, however, is enhanced by this long detention time.

OPERATION

Experience treating various types of textile waste including greige operations, dyeing waste from all types of dyes on cottons, wools, blends, synthetics, and mixtures; finishing wastes, including wash-and-wear treatments, mothproofing, resin treatment, fire retardant treatment; printing wastes including roller, flatbed, and screen; will indicate that no two wastes are exactly alike. General relationships hold true and reasonable efficiencies can be obtained without pilot work, but when high efficiencies are required and strict conditions must be met, each waste must be considered to have individual characteristics requiring evaluation. Due to this premise, off-the-shelf treatments cannot be expected to produce extremely desirable results at the least cost without some prior waste characterization and/or pilot plant data. Common sense will indicate that screening, lint removal, grease removal, and the like will be required in many cases. Wool waste cannot be treated if the grease from scouring is not removed prior to the biological step. Lint from cotton operations will clog diffusers, hang on mechanical aerators, and otherwise reduce efficiencies.

In some situations, segregation of the wastes will reduce the volume to treat. In others, the piping changes are so expensive that it may be more economical to handle the volume or reduce the amount of segregation used. It has been found that in many plants air can be used to provide neutralization of the alkaline waste through the production of CO_2 from biological activity and from CO_2 in the air. In other cases with certain dye mixtures, acid neutralization is required to produce acceptable color removal.

What we mean to say is that conditions must be maintained as optimum as is cost-effective to allow the biological matter to treat the many colored, strong textile wastes. Time has been used in place of chemicals, space, or area in place of concrete, and both in place of labor to produce the same or similar degree of treatment.

In selecting a treatment scheme, experience is valuable but the decision should be tempered by actual data. This data will aid in providing a much more sound and reasonable decision.

Consider the following four options as examples.

Medium strength waste -	Pretreatment (indirect discharge)
Medium strength waste -	Direct discharge
Concentrated waste -	Pretreatment (indirect discharge)
Concentrated waste -	Direct discharge

A reasonable evaluation of the wastes and sources of wastes will indicate that for most textile operations primary clarification is not required, however, screening for lint and rag removal is usually desirable and necessary.

Pilot plant data will determine the method of treatment that is expected to have the efficiency to produce the required effluent at an acceptable cost.

For pretreatment of a medium strength waste, an oxidation pond, extended aeration, bio-disc, or trickling filter should be given consideration. For direct discharge of this waste an oxygen system, extended aeration, or completely mixed activated sludge system should be considered. In all activated sludge evaluations prior to construction, detention time, solids level, sludge age, and F/M ratio should be varied and evaluated.

Pretreatment of a strong waste would probably omit the trickling filters and maybe the bio-disc as separate systems (depending on the waste's strength) and would consider oxidation ponds with mechanical aeration and recycle and either extended aeration or completely mixed activated sludge. Depending on whether solids removal is or is not provided will help adjust the detention time of pretreatment if activated sludge is desired. Direct discharge of strong wastes would normally limit the selection to include only an oxygen system, a completely mixed activated sludge system and an oxidation pond, or a bio-disc/activated sludge system or some other combination of these.

CONCLUSION

In summary, the use of biological treatment for textile wastes indicates that this process can be adapted to almost any textile wastes. There are various parameters or relationships that control this treatability, including F/M ratio, nutrient balance, MLSS concentrations, settleability of the sludge produced, wastes strength and makeup, recycle rate, and sludge age. These things all have levels that can be measured. The optimum blend then is determined for the wastes and results required. External factors such as power cost, changing requirements, and the so-called toxic limits all now affect the engineering decisions and must be evaluated as another variable.

Sludge removal aids in the increased efficiency of treatment by taking refractory organics, trace heavy metals, some residual color, hard to degrade organics, and degraded biomass from the biological system. This serves to enhance an active biological population by removing concentrations to potentially undesirable constituents which in turn increases the efficiency of the biological organisms.

To date, biological treatment has been the most successful treatment method developed for textile wastes and it should not be abandoned.

REFERENCES

1. Metcalf & Eddy, Inc., *Wastewater Engineering,* p. 503.
2. Sacramento State College, Department of Civil Engineering, *Operation of Wastewater Treatment Plants,* Chapter 9, p. 1.

A FUNDAMENTAL APPROACH TO APPLICATION OF REVERSE OSMOSIS FOR WATER POLLUTION CONTROL[*]

S. Sourirajan, Takeshi Matsuura[†]

Abstract

Reverse osmosis separation is the combined result of preferential sorption of one of the constituents of the feed solution at the membrane-solution interface, and mass transport by fluid permeation under pressure through the capillaries in the microporous membrane. Preferential sorption at the interface is a function of solute-solvent-membrane material interactions arising from polar (including ionic), steric, and nonpolar characters of each one of the components involved in the reverse osmosis system. Basic reverse osmosis transport equations, and available quantitative data on parameters characterizing polar, steric, and nonpolar interfacial forces applicable to reverse osmosis systems involving dilute aqueous solutions, preferential sorption of water at the membrane-solution interface, and a cellulose acetate (CA-398) or an aromatic polyamide-hydrazide copolymer (PPPH-8273) membrane material are presented. By integrating the latter parameters into the basic transport equations, one can predict the reverse osmosis performance of a membrane for a large number of feed solution systems involving inorganic and organic (ionized, nonionized, or partially ionized) solutes in aqueous solutions from only a single set of experimental data for a reference sodium chloride-water feed solution. This prediction technique is illustrated with respect to two specified membranes, one made of CA-398 material and the other made of PPPH-8273 material. The application of the above transport equations for predicting the performance of commercial reverse osmosis modules is also illustrated. Brief discussions on solute preferential sorption at membrane-solution interfaces, temperature effect, pH effect, membrane compaction effect, fouling problems, and ultrafiltration are also included with particular reference to application of reverse osmosis for water pollution control.

INTRODUCTION

Reverse osmosis in industry is a general process for the separation of substances in fluid (liquid or gaseous) solution by permeation under pressure through an appropriate synthetic membrane. Since the original development in 1960 of the now well known asymmetric porous cellulose acetate membranes for water desalination applications (ref. 1), many synthetic membranes have been successfully developed and tested for a variety of water pollution control applications (ref. 2). The operational simplicity and the obvious potential of reverse osmosis for many separation applications have generated a fast growing worldwide activity on the subject in recent years. In spite of such activity, reverse osmosis has not yet gained a major entry into the industrial world of water pollution control. This is not due to lack of sufficient interest in the application of reverse osmosis for water pollution control; but this is due to, at least, an apparent lack of such interest in a fundamental understanding of reverse osmosis itself, and in the assiduous development of an overall science of reverse osmosis (based on such understanding) necessary for its effective utilization with respect to any application, including water pollution control. Hence the object of this paper is to call attention to a fundamental approach to reverse osmosis research and development, and the science of reverse osmosis arising from that approach (ref. 3), and illustrate this approach by some quantitative data predicted by the application of this science. Such predictive capability is useful for the industrial development of reverse osmosis for water pollution control applications.

---

[*] Issued as N.R.C. No. 17022.

[†] National Research Council of Canada, Division of Chemistry, Ottawa, Canada.

THE APPROACH AND THE SCIENCE

The fundamental approach referred to above is the preferential sorption-capillary flow mechanism for reverse osmosis, which led to the development of the original porous cellulose acetate reverse osmosis membranes (ref. 1). According to this mechanism, which is discussed in detail in the literature (refs. 1,3,4,5), reverse osmosis separation is the combined result of preferential sorption of one of the constituents of the feed solution at the membrane-solution interface, and mass transport by fluid permeation under pressure through the capillaries of the microporous membrane. An appropriate chemical nature of the membrane surface on the feed solution side, and the existence of pores of appropriate size and number on the area of the membrane at the interface on that side together constitute the indispensable twin requirement for the practical success of this separation process. Thus for reverse osmosis separation to take place, one of the constituents of the feed solution must be preferentially sorbed at the membrane-solution interface; further, to be industrially useful, the reverse osmosis membrane must have a microporous and heterogeneous surface layer at all levels of solute separation, its entire porous structure must be asymmetric, and there should be no chemical reaction between the constituents of the feed solution and the material of the membrane surface. With an appropriate material for the membrane surface, practically any degree of solute separation is possible in reverse osmosis by simply changing the average pore size on the membrane surface and the operating conditions of the experiment. Aside from such process requirements, reverse osmosis is fundamentally not limited to any particular solvent, solute, membrane material, level of solute separation or that of solvent flux, or operating conditions of the experiment. Consequently, the overall science of reverse osmosis arising from the above approach unfolds itself through proper integration of the physicochemical factors governing preferential sorption of solvent or solute at membrane-solution interfaces, materials science of reverse osmosis membranes, and the engineering science of reverse osmosis transport, system analysis, and process design. While there is still a long way to go towards the full development of the science of reverse osmosis in all its aspects, significant progress has already been made, all of which is practically useful, which should be evident from the following discussion.

PREFERENTIAL SORPTION AT INTERFACES

Preferential sorption at the membrane-solution interface is a function of solute-solvent-membrane material (i.e., material of the membrane surface) interactions. These interactions arise in general from polar (hydrogen bonding), steric, nonpolar (hydrophobic), and/or ionic character of each one of the above components. The overall result of these interactions determines whether solvent or solute (or neither) is preferentially sorbed at the membrane-solution interface. Application of reverse osmosis to water pollution control may involve preferential sorption of water or solute at the membrane-solution interface depending on the chemical nature of solute and that of membrane material. When water is preferentially sorbed, reverse osmosis results in positive solute separation (i.e., solute concentration in the membrane permeated solution is less than that in the feed solution); when solute is preferentially sorbed, solute separation in reverse osmosis can be positive, negative, or zero, depending on the relative mobility of the solute species (compared to water) through the membrane pores under the conditions of the experiment. Both cases are illustrated in the literature (ref. 6).

MEMBRANE MATERIALS AND MEMBRANES

Though many membrane materials and membranes have been successfully tested for reverse osmosis applications (ref. 2), cellulose acetate (acetyl content ~39.8 percent, designated here as CA-398) membranes are still by far the most widely used ones in current industrial practice; these membranes are also the ones for which extensive scientific data have been generated. For this reason this paper is concerned mainly with such cellulose acetate membranes. Du Pont reverse osmosis modules are also widely used in industry; the membranes in these modules are made of an aromatic polyamide-hydrazide copolymer material (ref. 7), which is not commercially available for outside independent researchers. However, a chemically similar polymer (designated here as PPPH-8273) synthesized in the laboratory, has been studied as reverse osmosis membrane material, and a limited amount of scientific data has been generated for membranes made from the latter material (ref. 8) (which, for practical purposes, may be considered to be analogous to the Du Pont material); this paper also includes the latter data, and illustrates their utility.

The polymer materials CA-398 and PPPH-8273 have been chemically characterized in terms of their α_p (polar), α_n (nonpolar), and β (affinity for nonionized polar organic solutes relative to that for an ionized inorganic solute) parameters generated from liquid-solid chromatography (LSC) data (refs. 9,10). The relevance of such characterization to reverse osmosis stems from the principle that the solute-solvent-polymer material interactions governing the relative retention times of solutes in LSC are analogous to the interactions prevailing at the membrane-solution interface under reverse osmosis conditions. On arbitrarily defined relative scales (refs. 9,10), the values of α_p, α_n, and β are -1.00, -0.017, and 1.37 respectively for CA-398, and -0.31, 0.144, and 0.17 respectively for PPPH-8273 polymers. A higher value of α_p indicates stronger hydrogen bonding capacity of polymer material and hence its higher sorption capacity for water. A higher value of α_n for the polymer material results in greater mobility of the preferentially sorbed water through the membrane pores when water is preferentially sorbed, and lower mobility of the solute through the membrane pores when solute is preferentially sorbed at the membrane-solution interface; both these effects contribute to higher solute separation in reverse osmosis. A higher value of β denotes stronger affinity of the polymer for nonionized polar organic solutes (and consequently lesser preferential sorption of water at the membrane-solution interface) relative to ionized solutes. Thus the numerical values of α_p, α_n, and β direct attention to the inherent potential of polymer materials with relatively higher α_p and α_n values together with relatively lower β values (such as the case for PPPH-8273) for possible use in making high flux reverse osmosis membranes especially for applications requiring high separations of both ionized solutes and nonionized polar organic solutes in wastewaters.

Futher, with a given membrane material, an infinite number of membranes can be made with different porous structures and hence different reverse osmosis properties. The specific details of film casting techniques used in making the membranes decide the overall porous structure of the resulting membranes. For example, the aromatic polyamide membranes are usually cast at high temperatures (90° to 130° C) whereas the cellulose acetate membranes are usually cast at relatively low temperatures (0° to 30° C). The supermolecular polymer aggregates in a given casting solution are generally smaller in size at higher temperatures, which results ultimately in correspondingly smaller size pores on the membrane surface in the as-cast condition (ref. 11). Consequently, the use of higher temperatures for casting solution and/or casting atmosphere offers one of the several means of creating smaller average size of pores on the surface of resulting membranes. For some water pollution control applications, the practical possibility of using the above means of pore size generation on the membrane surface may be the deciding factor for the choice of membrane material, and the film casting conditions for making the required membranes.

PHYSICOCHEMICAL PARAMETERS CHARACTERIZING SOLUTES IN THE VICINITY OF INTERFACES

For reverse osmosis systems involving dilute aqueous feed solutions, three physicochemical parameters have been developed for characterizing ions and nonionized solutes in the vicinity of different membrane-solution interfaces. These parameters are: polar free energy parameter $-\Delta\Delta G/RT$, steric parameter $\delta^*\Sigma E_s$, and nonpolar parameter $\omega^*\Sigma s^*$. These parameters may be described briefly as follows.

Polar Free Energy Parameter $-\Delta\Delta G/RT$

When water is preferentially sorbed at the membrane-solution interface, $\Delta\Delta G/RT$ gives a quantitative measure of solute repulsion at the interface on a relative scale. This parameter was initially developed for inorganic ions, and later extended to nonionized polar organic solutes, organic ions, and inorganic ion pairs (refs. 8,12,13,14,15,16). The basis for this parameter arises from (1) Born equation for ion-solvent interaction (free energy of hydration, ΔG) as applied to the bulk feed solution phase and the membrane-solution interface, (2) the thermodynamic basis of Hammett and Taft equations representing the effect of structure on reaction rates and equilibria (ref. 17), (3) the relationship between the parameters of Taft eq. (16) in reference 17 and reverse osmosis data on solute transport parameter $D_{AM}/K\delta$ (defined by eq. (8) later in this discussion) for different solutes and membranes (refs. 18,19,20), and (4) the functional similarity of the thermodynamic quantity $\Delta\Delta F^{\ddagger}$ representing the transition state free energy change (ref. 17) and the quantity $\Delta\Delta G$ defined as

$$\Delta\Delta G = \Delta G_I - \Delta G_B, \qquad (1)$$

which represents the energy needed to bring an ion, or the nonionized solute molecule, from the bulk solution phase (subscript B) to the membrane-solution interface (subscript I). The quantity $-\Delta\Delta G/RT$, which is an interfacial property, is a function of the chemical nature of the solute, the solvent, and the membrane material, and it is independent of the porous structure of the membrane used. A lower value of $-\Delta\Delta G/RT$ for the solute yields a lower value for $D_{AM}/K\delta$ for the solute, and hence higher solute separation in reverse osmosis.

The values of $\Delta\Delta G$, and hence $-\Delta\Delta G/RT$, for different ions and nonionized polar organic solute molecules can be computed from data on ΔG_B (which arises from the physical chemistry of the bulk solution phase) and ΔG_I calculated from experimental reverse osmosis data on $D_{AM}/K\delta$ for different solutes (refs. 8,12,13,14, 15,16). Table 1 gives the available data on $-\Delta\Delta G/RT$ for several inorganic and organic ions, and inorganic ion-pairs for interfaces involving aqueous solutions and CA-398 or PPPH-8273 polymer membrane material. The value of $-\Delta\Delta G/RT$ for a completely ionized inorganic salt is simply the sum of the $-\Delta\Delta G/RT$ values for the ions involved. For example,

$$\left\{-\frac{\Delta\Delta G}{RT}\right\}_{NaCl} = \left\{-\frac{\Delta\Delta G}{RT}\right\}_{Na^+} + \left\{-\frac{\Delta\Delta G}{RT}\right\}_{Cl^-}$$

$$\left\{-\frac{\Delta\Delta G}{RT}\right\}_{Mg(NO_3)_2} = \left\{-\frac{\Delta\Delta G}{RT}\right\}_{Mg^{++}} + 2\left\{-\frac{\Delta\Delta G}{RT}\right\}_{NO_3^-} .$$

For nonionized polar organic solutes, the values of ΔG_B and ΔG_I are simply the additive functions of the contributions (γ_B and γ_I respectively) of the structural groups in the molecule, so they can be expressed as:

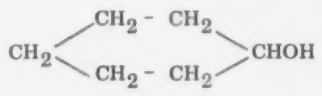
$$\Delta G_B = \Sigma\gamma_B\,(\text{structural group}) + \gamma_{B,0} \text{ and} \qquad (2)$$

$$\Delta G_I = \Sigma\gamma_I\,(\text{structural group}) + \gamma_{I,0}. \qquad (3)$$

For example, for s-butyl alcohol whose molecular formula is $CH_3CH_2CH(OH)CH_3$

$$\left\{-\frac{\Delta\Delta G}{RT}\right\} = -\frac{1}{RT}\Big[\big\{2\gamma_I\,(CH_3) + \gamma_I\,(CH_2) + \gamma_I\,(CH) + \gamma_I\,(OH) + \gamma_{I,0}\big\} - \big\{2\gamma_B\,(CH_3) + \gamma_B\,(CH_2) + \gamma_B\,(CH) + \gamma_B\,(OH) + \gamma_{B,0}\big\}\Big];$$

for cyclohexanol whose molecular structure is



$$-\frac{\Delta\Delta G}{RT} = -\frac{1}{RT}\Big[\big\{5\gamma_1(CH_2) + \gamma_1(CH) + \gamma_I(OH) + \gamma_I(\text{cyclic, 6-membered}) + \gamma_{I,0}\big\} - \big\{5\gamma_B(CH_2) + \gamma_B(CH) + \gamma_B(OH) + \gamma_B(\text{cyclic, 6-membered}) + \gamma_{B,0}\big\}\Big];$$

interface on a relative scale. This parameter was initially developed for inorganic ions, and later extended to nonionized polar organic solutes, organic ions, and inorganic ion pairs (refs. 8,12,13,14,15,16). The basis for this parameter arises from (1) Born equation for ion-solvent interaction (free energy of hydration, ΔG) as applied to the bulk feed solution phase and the membrane-solution interface, (2) the thermodynamic basis of Hammett and Taft equations representing the effect of structure on reaction rates and equilibria (ref. 17), (3) the relationship between the parameters of Taft eq. (16) in reference 17 and reverse osmosis data on solute transport parameter $D_{AM}/K\delta$ (defined by eq. (8) later in this discussion) for different solutes and membranes (refs. 18,19,20), and (4) the functional similarity of the thermodynamic quantity $\Delta\Delta F^{\ddagger}$ representing the transition state free energy change (ref. 17) and the quantity $\Delta\Delta G$ defined as

$$\Delta\Delta G = \Delta G_I - \Delta G_B, \qquad (1)$$

which represents the energy needed to bring an ion, or the nonionized solute molecule, from the bulk solution phase (subscript B) to the membrane-solution interface (subscript I). The quantity $-\Delta\Delta G/RT$, which is an interfacial property, is a function of the chemical nature of the solute, the solvent, and the membrane material, and it is independent of the porous structure of the membrane used. A lower value of $-\Delta\Delta G/RT$ for the solute yields a lower value for $D_{AM}/K\delta$ for the solute, and hence higher solute separation in reverse osmosis.

The values of $\Delta\Delta G$, and hence $-\Delta\Delta G/RT$, for different ions and nonionized polar organic solute molecules can be computed from data on ΔG_B (which arises from the physical chemistry of the bulk solution phase) and ΔG_I calculated from experimental reverse osmosis data on $D_{AM}/K\delta$ for different solutes (refs. 8,12,13,14, 15,16). Table 1 gives the available data on $-\Delta\Delta G/RT$ for several inorganic and organic ions, and inorganic ion-pairs for interfaces involving aqueous solutions and CA-398 or PPPH-8273 polymer membrane material. The value of $-\Delta\Delta G/RT$ for a completely ionized inorganic salt is simply the sum of the $-\Delta\Delta G/RT$ values for the ions involved. For example,

$$\left\{-\frac{\Delta\Delta G}{RT}\right\}_{NaCl} = \left\{-\frac{\Delta\Delta G}{RT}\right\}_{Na^+} + \left\{-\frac{\Delta\Delta G}{RT}\right\}_{Cl^-}$$

$$\left\{-\frac{\Delta\Delta G}{RT}\right\}_{Mg(NO_3)_2} = \left\{-\frac{\Delta\Delta G}{RT}\right\}_{Mg^{++}} + 2\left\{-\frac{\Delta\Delta G}{RT}\right\}_{NO_3^-}.$$

For nonionized polar organic solutes, the values of ΔG_B and ΔG_I are simply the additive functions of the contributions (γ_B and γ_I respectively) of the structural groups in the molecule, so they can be expressed as:

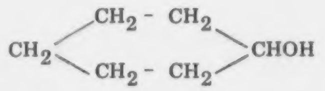
$$\Delta G_B = \Sigma\gamma_B\,(\text{structural group}) + \gamma_{B,0} \text{ and} \qquad (2)$$

$$\Delta G_I = \Sigma\gamma_I\,(\text{structural group}) + \gamma_{I,0}. \qquad (3)$$

For example, for s-butyl alcohol whose molecular formula is $CH_3CH_2CH(OH)CH_3$

$$\left\{-\frac{\Delta\Delta G}{RT}\right\} = -\frac{1}{RT}\Big[\big\{2\gamma_I\,(CH_3) + \gamma_I\,(CH_2) + \gamma_I\,(CH) + \gamma_I\,(OH) + \gamma_{I,0}\big\} - \big\{2\gamma_B\,(CH_3) + \gamma_B\,(CH_2) + \gamma_B\,(CH) + \gamma_B\,(OH) + \gamma_{B,0}\big\}\Big];$$

for cyclohexanol whose molecular structure is



$$-\frac{\Delta\Delta G}{RT} = -\frac{1}{RT}\Big[\big\{5\gamma_I(CH_2) + \gamma_I(CH) + \gamma_I(OH) + \gamma_I(\text{cyclic, 6-membered}) + \gamma_{I,0}\big\} - \big\{5\gamma_B(CH_2) + \gamma_B(CH) + \gamma_B(OH) + \gamma_B(\text{cyclic, 6-membered}) + \gamma_{B,0}\big\}\Big];$$

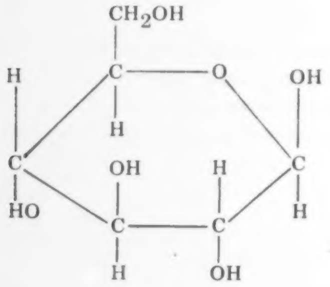
TABLE 1. DATA ON FREE ENERGY PARAMETER ($-\Delta\Delta G/RT$) FOR SOME IONS AND ION-PAIRS AT 25° C, APPLICABLE FOR INTERFACES INVOLVING DILUTE AQUEOUS SOLUTIONS AND CA-398 OR PPPH-8273 POLYMER MEMBRANE MATERIAL

Species	($-\Delta\Delta G/RT$)		Species	($-\Delta\Delta G/RT$)		Species	($-\Delta\Delta G/RT$)	
	CA-398	PPPH-8273		CA-398	PPPH-8273		CA-398	PPPH-8273
Inorganic cations			Inorganic anions (con.)			Organic ions		
H^+	6.34		I^-	−3.98	1.33	$HCOO^-$	−4.78	
Li^+	5.77	−1.20	IO_3^-	−5.69		H Phthalate$^-$	−4.63	
Na^+	5.79	−1.35	$H_2PO_4^-$	−6.16		$C_2O_4^{2-}$	−14.06	
K^+	5.91	−1.28	BrO_3^-	−4.89		t-$C_4H_9COO^-$	−6.90	
Rb^+	5.86	−1.27	NO_2^-	−3.85		i-$C_3H_7COO^-$	−6.11	
Cs^+	5.72	−1.23	NO_3^-	−3.66	2.54	cyclo-$C_6H_{11}COO^-$	−6.24	
NH_4^+	5.97		ClO_3^-	−4.10		n-$C_4H_9COO^-$	−6.11	
Mg^{2+}	8.72	−2.41	ClO_4^-	−3.60		n-$C_3H_7COO^-$	−6.06	
Ca^{2+}	8.88		HCO_3^-	−5.32		$C_2H_5COO^-$	−6.14	
Sr^{2+}	8.76		HSO_4^-	−6.21		CH_3COO^-	−5.95	1.33
Ba^{2+}	8.50		SO_4^{2-}	−13.20	2.18	$C_6H_5(CH_3)_2COO^-$	−5.93	
Mn^{2+}	8.58		$S_2O_3^{2-}$	−14.03		$C_6H_5(CH_2)_2COO^-$	−5.86	
Co^{2+}	8.76		SO_3^{2-}	−13.12		$C_6H_5(CH_2)COO^-$	−5.69	
Ni^{2+}	8.47		CrO_4^{2-}	−13.69		$C_6H_5COO^-$	−5.66	
Cu^{2+}	8.41		$Cr_2O_7^{2-}$	−11.16		p-$CH_3OC_6H_4COO^-$	−5.74	
Zn^{2+}	8.76		CO_3^{2-}	−13.22		m-$CH_3C_6H_4COO^-$	−5.67	
Cd^{2+}	8.71		$Fe(CN)_6^{3-}$	−20.87		m-$OHC_6H_4COO^-$	−5.64	
Pb^{2+}	8.40		$Fe(CN)_6^{4-}$	−26.83		p-$ClC_6H_4COO^-$	−5.63	
Fe^{2+}	9.33					m-$NO_2C_6H_4COO^-$	−5.92	
Fe^{3+}	9.82		Inorganic ion-pairs‡			p-$NO_2C_6H_4COO^-$	−5.93	
Al^{3+}	10.41		$MgSO_4$	3.45		o-$ClC_6H_4COO^-$	−6.41	
Ce^{3+}	10.62		$CoSO_4$	3.41		o-$NO_2C_6H_4COO^-$	−6.61	
Cr^{3+}	11.28		$ZnSO_4$	2.46		$HOOCCOO^-$	−6.60	
La^{3+}	12.89		$MnSO_4$	2.48		$HOOCCH_2COO^-$	−6.46	
Th^{4+}	12.42		$CuSO_4$	2.85		$HOOC(CH_2)_2COO^-$	−5.65	
			$CdSO_4$	3.04		$CH_3CHOHCOO^-$	−6.30	
Inorganic anions			$NiSO_4$	2.18		$HOOCCH(OH)CH_2COO^-$	−5.97	
OH^-	−6.18		$KFe(CN)_6^{2-}$	−2.53		$HOOCCH(OH)CH(OH)COO^-$	−6.40	
F^-	−4.91	1.03	$KFe(CN)_6^{3-}$	−17.18		$HOOCCH_2C(OH)(COOH)CH_2COO^-$	−6.24	
Cl^-	−4.42	1.35						
Br^-	−4.25	1.35						

‡ Applicable data on dissociation equilibrium constant are given below:

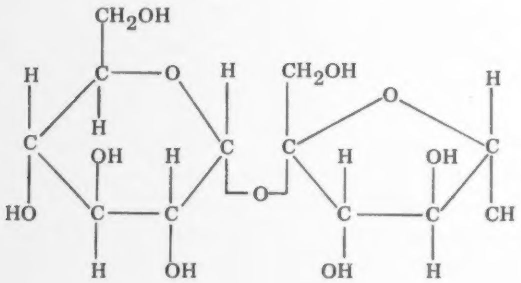
Solute	Dissociation equilibrium constant (ref. 21)	Solute	Dissociation equilibrium constant
$MgSO_4$	4.36×10^{-3}	$CuSO_4$	2.62×10^{-4}
$CoSO_4$	3.38×10^{-3}	$CdSO_4$	4.89×10^{-3}
$ZnSO_4$	4.89×10^{-3}	$NiSO_4$	3.98×10^{-3}
$MnSO_4$	5.20×10^{-3}	$K_3Fe(CN)_6$	3.98×10^{-2}
		$K_4Fe(CN)_6$	5.01×10^{-3}

for D-glucose whose molecular structure is



$$\left\{-\frac{\Delta\Delta G}{RT}\right\} = -\frac{1}{RT}\Big[\{\gamma_1(CH_2) + 5\gamma_1(CH)$$
$$+ 5\gamma_I(OH)$$
$$+ \gamma_I(\text{cyclic, 6-membered})$$
$$+ \gamma_I(O) + \gamma_{I,0}\} - \{\gamma_B(CH_2)$$
$$+ 5\gamma_B(CH + 5\gamma_B(OH)$$
$$+ \gamma_B(\text{cyclic, 6-membered})$$
$$+ \gamma_B(O) + \gamma_{B,0}\}\Big];$$

and for sucrose whose molecular structure is



$$\left\{-\frac{\Delta\Delta G}{RT}\right\} = -\frac{1}{RT}\Big[\{3\gamma_I(CH_2) + 8\gamma_I(CH)$$
$$+ \gamma_I(C) + \gamma_I(\text{cyclic, 6-membered})$$
$$+ \gamma_I(\text{cyclic, 5-membered})$$
$$+ 8\gamma_I(OH) + 3\gamma_I(O)$$
$$+ \gamma_{I,0}\} - \{3\gamma_B(CH_2)$$
$$+ 8\gamma_B(CH) + \gamma_B(C)$$
$$+ \gamma_B(\text{cyclic, 6-membered})$$
$$+ \gamma_B(\text{cyclic, 5-membered})$$
$$+ 8\gamma_B(OH) + 3\gamma_B(O) + \gamma_{B,0}\}\Big].$$

The available values of γ_B and γ_I for different structural groups and the applicable constants $\gamma_{B,0}$ and $\gamma_{I,0}$ for interfaces involving aqueous solutions and CA-398 or PPPH-8273 polymer membrane material are listed in Table 2.

TABLE 2. STRUCTURAL GROUP CONTRIBUTIONS FOR ΔG_B AND ΔG_I AT 25° C, APPLICABLE FOR INTERFACES INVOLVING DILUTE AQUEOUS SOLUTIONS AND CA-398 OR PPPH-8273 POLYMER MEMBRANE MATERIAL

$\gamma_{B,0} = -12.04$; $\gamma_{I,0} = -41.21$ for CA-398, and 44.01 for PPPH-8273

Structural group	γ_B	γ_I CA-398	γ_I PPPH-8273
- CH	11.07	24.23	- 17.74
>CH	0.17	0.24	0.32
⩾CH	-10.62	-23.65	18.41
>C<	-21.50	-47.39	36.26
Cyclic (5-membered)	20.60	46.99	–
Cyclic (6-membered)	20.49	47.12	-37.37
- OH	3.99	17.04	-25.21
>O	- 4.03	- 4.59	- 4.21
- CN	5.19	17.17	–
>C=O	- 5.80	- 6.32	- 6.11
- CHO	5.80	18.84	-23.36
- COOH	2.49	15.13	–
- NO_2	6.56	18.95	–
- $CONH_2$	-0.21	12.75	–
- C_6H_5	8.41	21.43	-20.09
- COO-	-5.14	-6.32	-5.49

Steric Parameter $\delta^*\Sigma E_s$

The electrostatic repulsion of ions in aqueous solution in the vicinity of membrane materials of low dielectric constant (ref. 22) is much larger in magnitude than repulsions or attractions resulting from interfacial forces due to steric and nonpolar (hydrophobic) effects; hence the latter two effects are significant only for reverse osmosis systems involving nonionized solutes. Steric hindrance to reactivity of molecules arises from repulsions between nonbonded atoms, and also from interference of groups or atoms with each other's motions: consequently steric hindrance (which also parallels the effective size of the molecules concerned) is always a repulsive force at the interface. The parameter $\delta^*\Sigma E_s$ represents the total steric effect affecting solute transport through the porous membrane in reverse osmosis (ref. 19); steric hindrance to such solute transport results in a negative value for the parameter $\delta^*\Sigma E_s$, which contributes to higher solute separation in reverse osmosis. Unlike the polar free energy parameter $(-\Delta\Delta G/RT)$, the steric parameter $\delta^*\Sigma E_s$ is a function not only of the chemical nature of the solute, the solvent and the membrane material, but it is also a function of the porous structure of the membrane surface.

With respect to solute molecules involving monofunctional groups, the value of the steric constant ΣE_s for the substituent group in the polar organic molecule can be computed as the summation of the steric substituent constants for the structural units involved from the data on E_s given by Taft (listed in Table 3) (refs. 17,19). For example, ΣE_s for the substituent group in t-butyl alcohol = E_s for t-C_4H_9; that for cyclohexanol = E_s for cyclo-C_6H_{11}; that for t-butyl isopropyl ether = E_s for t-C_4H_9 + E_s for i-C_3H_7; and that for diisopropyl ketone = 2 × E_s for i-C_3H_7, etc. It must be noted that the value of ΣE_s for the substituent group in the solute molecule depends only on the chemical nature of the group, and represents the property of the solute in the bulk solution phase. The steric coefficient δ^* associated with ΣE_s, however, depends on the chemical nature of the functional group in the solute molecule, as well as the chemical nature and porous structure of the membrane surface. The available values of δ^* for alcohol-, aldehyde-, ketone-, and ether solutes (refs. 8,13) for CA-398 and PPPH-8273 membrane materials are given in Figure 1 as a function of average pore size on the membrane surface as represented by the quantity $\ln(C^*_{NaCl}/A)$. Using the values of E_s given by Taft (ref. 17) and suitable interpolation techniques, additional such data have been generated for practical use in reverse osmosis (refs. 19,23); some of these data are also included in Table 3.

For solute molecules involving polyfunctional groups (for example, glucose, sucrose, etc.), there is no simple way by which the values of ΣE_s can be computed from data given

TABLE 3. TAFT'S STERIC SUBSTITUENT CONSTANTS, E_s at 25° C APPLICABLE FOR AQUEOUS SOLUTIONS AND SOLUTE MOLECULES INVOLVING MONOFUNCTIONAL GROUPS (refs. 17,19)

Substituent group	E_s	Substituent group	E_s
Aliphatic compounds			
CH_3	0.00	cyclo-C_7H_{13}	-1.10
C_2H_5	-0.07	$(CH_3)(C_6H_5)CH$	-1.19
Cyclo-C_4H_7	-0.06	t-C_4H_9	-1.54
n-C_3H_7	-0.36	$(C_6H_5)(C_2H_5)CH$	-1.50
n-C_4H_9	-0.39	t-$C_4H_9CH_2$	-1.74
n-C_5H_{11}	-0.40	$(C_6H_5)_2CH$	-1.76
i-C_5H_{11}	-0.35	(CH_3)(neopentyl)CH	-1.85
n-C_8H_{17}	-0.33	$(C_2H_5)_2CH$	-1.98
t-$C_4H_9CH_2CH_2$	-0.34	(n-$C_3H_7)_2CH$	-2.11
$C_6H_5CH_2$	-0.38	(i-$C_4H_9)_2CH$	-2.47
$C_6H_5CH_2CH_2$	-0.38	$(CH_3)_2$(neopentyl)C	-2.57
$C_6H_5CH_2CH_2CH_2$	-0.45	(neopentyl)$_2$CH	-3.18
i-C_3H_7	-0.70	(CH_3)(t-C_4H_9)CH	-3.33
cyclo-C_5H_9	-0.51	$(CH_3)_2$(t-C_4H_9)C	-3.9
cyclo-C_6H_{11}	-0.79	$(C_2H_5)_3C$	-3.8
i-C_4H_9	-0.93	(CH_3)(t-C_4H_9)(neopentyl)C	-4.0
cyclo-$C_6H_{11}CH_2$	-0.98	(n-$C_4H_9)_2CH$	-2.13
$(CH_3)(C_2H_5)CH$	-1.13	(t-$C_4H_9)_2CH$	-3.00

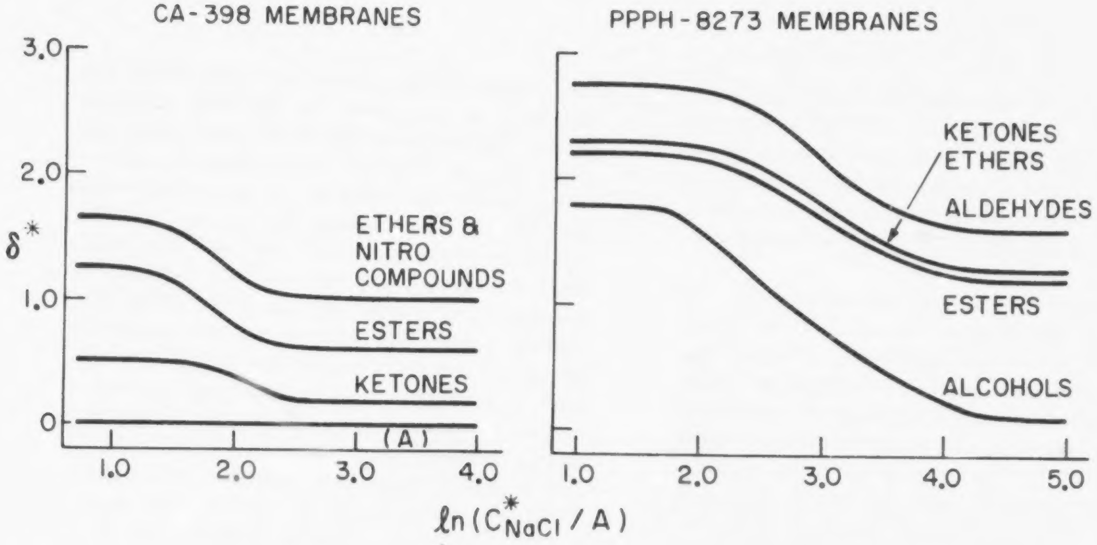


Figure 1. Correlation of δ^* versus $\ln(C^*_{NaCl}/A)$ for CA-398 and PPPH-8273 membranes at 25° C. Line A in Figure is applicable to alcohol-, aldehyde-, amide-, and undissociated carboxylic acid solutes.

in Table 3. For such solutes, an empirical method has been established (ref. 13) for estimating the value of the parameter $\delta^*\Sigma E_s$ on the basis that the latter reaches a limiting value, designated as $(\delta^*\Sigma E_s)_{lim}$, when the average pore size on the membrane surface becomes sufficiently small. For a given membrane material, this quantity $(\delta^*\Sigma E_s)_{lim}$ is simply an additive function of the contribution ϕ of each of the structural units involved in the solute molecule, so that

$$(\delta^*\Sigma E_s)_{lim} = \Sigma\phi(\text{structural unit}) + \phi_o. \tag{4}$$

Table 4 lists the available data (refs. 13,24) on ϕ and ϕ_o applicable for aqueous solutions involving polyfunctional solutes and CA-398 membrane material. For illustration, from the molecular structures of D-glucose and sucrose given above,

$$\begin{aligned}(\delta^*\Sigma E_s)_{lim} &\text{ for D-glucose}\\ &= \phi(CH_2) + 5\phi(CH) + 5\phi(OH)\\ &\quad + \phi(\text{cyclic, 6-membered, and single ring}) + \phi(O)\\ &\quad + \phi_o\end{aligned}$$

and

$$\begin{aligned}(\delta^*\Sigma E_s)_{lim} &\text{ for sucrose}\\ &= 3\phi(CH_2) + 8\phi(CH) + \phi(C)\\ &\quad + \phi(\text{cyclic, 6-membered, and two rings})\\ &\quad + \phi(\text{cyclic, 5-membered, and two rings}) + 8\phi(OH) + 3\phi(O) + \phi_o.\end{aligned}$$

The applicable value of $\delta^*\Sigma E_s$ for the particular membrane used can then be computed from the data on $(\delta^*\Sigma E_s)_{lim}$ obtained as illustrated above, and the correlation given in Figure 2, which relates the ratio $(\delta^*\Sigma E_s)/(\delta^*\Sigma E_s)_{lim}$ and the average pore size on the membrane surface as represented by the quantity $\ln(C^*_{NaCl}/A)$.

Nonpolar Parameter $\omega^*\Sigma s^*$

This parameter represents the hydrophobic force at the membrane-solution interface. A direct measure of hydrophobicity or nonpolar character of a hydrocarbon molecule is given either by its molar solubility in water or by its molar attraction constant as given by Small's number (ref. 25). A decrease in solubility or increase in Small's number signifies an increase in hydrophobicity or nonpolar character for the

TABLE 4. STRUCTURAL GROUP CONTRIBUTIONS FOR $(\delta^*\Sigma E_s)_{lim}$ FOR SOLUTE MOLECULES WITH POLYFUNCTIONAL GROUPS AT 25° C, APPLICABLE FOR INTERFACES INVOLVING DILUTE AQUEOUS SOLUTIONS AND CA-398 POLYMER MEMBRANE MATERIAL

$\phi_0 = -4.83$ for CA-398

Structural unit	ϕ
$-CH_3$	2.90
$>CH_2$	-0.02
$\gtrdot CH$	-3.19
$-\overset{\vert}{\underset{\vert}{C}}-$	-6.88
Cyclic (5-membered and single ring)	5.22
Cyclic (6-membered and single ring)	4.70
Cyclic (5-membered and two rings)	5.99
Cyclic (6-membered and two rings)	5.47
$-OH$	2.01
$>O$	0.63
$>C=O$	-1.15
$-CHO$	2.14

hydrocarbon. The Small's number versus logarithm of solubility is a straight line which is different for different reactive series of compounds of similar chemical nature including paraffins, cycloparaffins, olefins, cycloolefins, diolefins, acetylenes, and aromatics. By adjusting the data on Small's number for various structural groups such that the correlation of Small's number for the paraffin hydrocarbon (taken as reference) versus logarithm of its molar solubility in water is valid for hydrocarbons in all the above reactive series, a modified number for the molar attraction constant, called the "modified Small's number" represented by s*, has been generated for different structural groups (ref. 26) as given in Table 5. The modified Small's number Σs^* for a hydrocarbon molecule, or the substituent group in a polar organic molecule, is obtained from its chemical structure using the additive property of s* for different structural groups. For example,

$$\Sigma s^*(C_6H_6) = s^*(C_6H_5) + s^*(H)$$

$$\Sigma s^*(C_6H_4(CH_3)_2) = s^*(C_6H_4) + 2s^*(CH_3)$$

$$\Sigma s^*(\underbrace{CH = CHCH_2CH_2CH_2}) = 2s^*(-CH=) + 3(>CH_2)$$

$$\Sigma s^*(\underbrace{CH = CH - CH = CH - CH = CH - CH_2}) = 6s^*(-CH=) + s^*(>CH_2) + s^*(\text{conjugation})$$

Σs^* for the substituent group in CH_3OH
$= s^*(CH_3)$

Σs^* for the substituent group in $CH_3(CH_2)_2CH(CH_3)CH_2OH$
$= 2s^*(CH_3) + 3s^*(>CH_2) + s^*(\gtrdot CH)$

Σs^* for the substituent group in $(CH_3)_3COH$
$= 3s^*(CH_3) + s^*(>C<)$

Σs^* for the substituent group in $\underbrace{(CH_2)_5CH(OH)}$
$= 5s^*(>CH_2) + s^*(\gtrdot CH)$

etc. The scale of Σs^* is consistent within each of the groups of aromatic, cyclic, and noncyclic hydrocarbon structure. Just as ΣE_s, Σs^* represents the property of the solute in the bulk solution phase.

The coefficient ω^* associated with Σs^* in the nonpolar parameter is a function of the chemical nature of the interface and independent of the porous structure of the membrane surface. For interfaces involving aqueous solutions, C_1 to C_9 monohydric alcohol-solutes and CA-398 or PPPH-8273 polymer membrane material, the available values of ω^* obtained experimentally (ref. 27) are listed in Table 6.

Referring to Table 6, the value of ω^* is a function of both the number of carbon atoms and degree of branching in the molecular structure of the alcohol-solute. The quantity Δs^*, defined as

$$\Delta s^*(\text{alcohol}) = \Sigma s^*(\text{alcohol}) - \Sigma s^*(\text{straight chain primary alcohol with the same number of carbon atoms}) \qquad (5)$$

serves as a quantitative measure of the latter variable. As the degree of branching increases, the value of Δs^* becomes more negative. An increase in the value of ω^* denotes greater nonpolar attraction of the solute towards the membrane surface, whereas a decrease in ω^* denotes lesser such attraction. This is under-

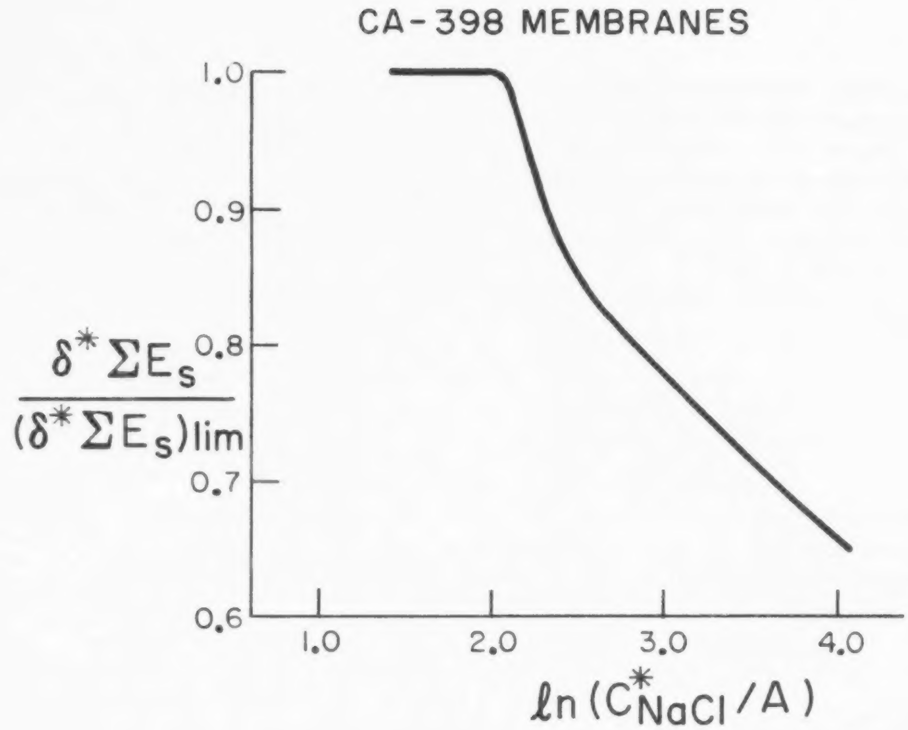


Figure 2. Correlation of $\delta^* \Sigma E_s/(\delta^* \Sigma E_s)_{\text{lim}}$ versus $\ln(C^*_{NaCl}/A)$ for CA-398 and PPPH-8273 membranes at 25° C.

standable on the basis of the solubility of alcohol in water, which increases with increase in the degree of branching in the molecular structure of the alcohol. An increase in solubility in water means greater solute-solvent attraction, which tends to decrease the solute-polymer attraction, and this is expressed by a decrease in ω^*. Thus the data given in Table 6 show that while an increase in carbon number tends to increase the value of ω^*, the opposite effect is the case as the Δs^* value becomes more negative. When these opposing values

TABLE 5. MODIFIED SMALL'S NUMBER s^* (IN $\text{cal}^{1/2}\text{cc}^{1/2}\text{g-mole}^{-1}$) FOR SOME ORGANIC STRUCTURAL GROUPS AT 25° C APPLICABLE FOR DILUTE AQUEOUS SOLUTIONS (ref. 26)

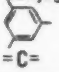
Structural group		s^*	Structural group		s^*	Structural group	s^*
$-CH_3$	single bonded	214	$CH_2=$	double bonded	140	Phenylene (o,m,p)	258
$>CH_2$		133	$-CH=$		61	Ring (5-membered)	0
$>CH$		28	$>C=$		-31	Ring (6-membered)	0
$>C<$		-93	$CH\equiv C-$		-15	Conjugation	25
H		90	$-C\equiv C-$		-78		181
			Phenyl		335	$=C=$	-31

TABLE 6. DATA ON ω^* (IN THE NONPOLAR PARAMETER $\omega^*\Sigma s^*$) AT 25° C APPLICABLE FOR INTERFACES INVOLVING C_1-C_9 MONOHYDRIC ALCOHOL-SOLUTES, DILUTE AQUEOUS SOLUTIONS, AND CA-398 OR PPPH-8273 POLYMER MEMBRANE MATERIAL

Δs^*(alcohol)	CA-398		PPPH-8273	
	n_c	$\omega^* \times 10^3$	n_c	$\omega^* \times 10^3$
0	1 to 3	0	1 to 4	0
−24	3 to 5	0	3 and 4	0
−48	6 and 7	0	6 and 7	−0.84
0	4 to 8	2.1	5 to 9	0.55
−24	6 to 9	1.2	5 to 7	−0.28
−64;−72	4 to 7	−1.0	7	−1.35
88	6 and 7	−2.2	6 and 7	−1.35

NOTES: ω^* in $cal^{-1/2}cc^{-1/2}$g-mole.

n_c = number of carbon atoms in the alcohol molecule.

Δs^* (alcohol) = Σs^*(alcohol) − Σs^* (straight chain primary alcohol with the same n_c). For example,

$$\Delta s^*(CH_3CHOHCH_3) = \Sigma s^*(CH_3CHOHCH_3) - \Sigma s^*(CH_3CH_2CH_2OH)$$
$$= 456 - 480 = -24$$

cancel each other ω^* becomes zero. An explanation for the negative values for ω^* is in order; this is simply a matter of scale which arbitrarily sets $\omega^* = 0$ for solute molecules containing no more than three straight chain carbon atoms not associated with a polar functional group.

TRANSPORT EQUATIONS FOR REVERSE OSMOSIS SYSTEMS INVOLVING AQUEOUS SOLUTIONS AND PREFERENTIAL SORPTION OF WATER AT THE MEMBRANE-SOLUTION INTERFACE

Basic Equations

At any given operating temperature and pressure, the experimental reverse osmosis data on pure water permeation rate *(PWP)*, product rate *(PR)*, and fraction solute separation *f* at any point (position or time) in the reverse osmosis system can be analyzed on the basis that *PWP* is directly proportional to the operating pressure, the solvent water transport (N_B) through the membrane is proportional to the effective pressure, the solute transport (N_A) through the membrane is due to pore diffusion through the membrane capillaries and hence proportional to the concentration difference across the membrane, and the mass transfer coefficient k on the high pressure side of the membrane is given by the "film" theory on mass transport. This analysis, which is applicable to all membrane materials and membranes at all levels of solute separation, gives rise to the following basic reverse osmosis transport equations (ref. 1):

$$A = (PWP)/M_B \times S \times 3600 \times P \tag{6}$$

$$N_B = A[P - \pi(X_{A2}) + \pi(X_{A3})] \tag{7}$$

$$= \left\{\frac{D_{AM}}{K\delta}\right\}\left\{\frac{1 - X_{A3}}{X_{A3}}\right\}(c_2X_{A2} - c_3X_{A3}) \tag{8}$$

$$= kc_1(1 - X_{A3}) \ln \left\{\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right\} . \tag{9}$$

In this analysis, the low pressure side of the membrane is assumed to be at atmospheric pressure, and the operating pressure P is given in gauge pressure. Under steady state operating conditions, a single set of experimental data on *PWP, PR,* and *f* enables one to calculate the quantities A, X_{A2}, $D_{AM}/K\delta$, and k at any point in the reverse osmosis system using equations (6) to (9); the transport parameter

$D_{AM}/K\delta$ is treated as a single quantity for purposes of analysis (ref. 1).

It must be emphasized that neither any one equation in the set of equations (6) to (9), nor any part of this set of equations, is adequate representation of reverse osmosis transport; the latter is governed simultaneously by the entire set of equations (6) to (9).

Correlations of A, $D_{AM}/K\delta$, and k

The correlations of these quantities with operating pressure, temperature, feed concentration, feed flow rate, nature of solute and membrane compaction during continuous operation are of practical interest from the point of view of specifying membranes and predicting membrane performance under different experimental conditions. Such correlations are best established experimentally for different membrane materials, membranes, and solutes. The following correlations so established are used in obtaining the results presented in this paper.

1. For CA-398 membranes, $D_{AM}/K\delta$ for a given solute (whether ionized or nonionized) is independent of feed concentration and feed flow rate.
2. For PPPH-8273 membranes, $D_{AM}/K\delta$ for any nonionic solute is independent of feed concentration and feed flow rate; in limited range of concentrations, $D_{AM}/K\delta$ is also independent of X_{A2} for ionized solutes involving divalent ions; and for ionized solutes involving monovalent ions only,

$$D_{AM}/K\delta \propto X_{A2}^{-0.2} \; . \qquad (10)$$

3. With respect to any given membrane, k for any solute (k_{solute}) can be obtained from the corresponding value of k for NaCl (k_{NaCl}) for a reference NaCl-H_2O feed solution using the relation:

$$k_{solute} = k_{NaCl} \left[(D_{AB})_{solute}/(D_{AB})_{NaCl}\right]^{2/3} \qquad (11)$$

where $(D_{AB})_{solute}$ and $(D_{AB})_{NaCl}$ are the diffusivities of the solute in the feed solution under consideration, and NaCl in reference feed solution respectively.

Membrane Specifications

At a specified operating temperature and pressure, a reverse osmosis membrane can be specified in terms of its performance data with respect to a reference solute in aqueous solution. For the purpose of this paper, NaCl is taken as the reference solute. Any CA-398 membrane can be completely specified in terms of its A and $(D_{AM}/K\delta)_{NaCl}$ values; any PPPH-8273 membrane can be completely specified in terms of its values for A and $(D_{AM}/K\delta)_{NaCl}$ corresponding to a given X_{A2} value. A single set of experimental reverse osmosis data on *PWP*, *PR*, and *f* for a reference NaCl-H_2O feed solution under known operating conditions is enough for use in equations (6) to (9) to obtain the required specifying data on A, $(D_{AM}/K\delta)_{NaCl}$, and X_{A2}. When a membrane is so specified, its reverse osmosis performance with respect to a large number of inorganic and organic solutes, and different feed concentrations and feed flow rates (as expressed by different k values) at the specified pressure and temperature can be predicted from the basic transport equations or by combining them with the polar free energy, steric, and nonpolar parameters given above. This predicion technique is outlined and illustrated below with respect to a CA-398 membrane and a PPPH-8273 membrane specified as in Table 7.

Predictive Capability of Basic Transport Equations

Combining equations (7), (8), and (9),

$$A[P - \pi(X_{A2}) + \pi(X_{A3})] = \left\{\frac{D_{AM}}{K\delta}\right\}\left\{\frac{1 - X_{A3}}{X_{A3}}\right\}(c_2X_{A2} - c_3X_{A3}) \qquad (12)$$

$$\frac{(c_2X_{A2} - c_3X_{A3})}{X_{A3}} = \frac{k}{(D_{AM}/K\delta)}\, c_1 \ln\left\{\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right\} \qquad (13)$$

TABLE 7. MEMBRANE SPECIFICATIONS
Operating pressure: 405 psig (27.56 atm)
Operating temperature: 25° C

	CA-398 Membrane	PPPH-8273 Membrane
A, g-mole $H_2O/cm^2 s$ atm	1.660×10^{-6}	1.300×10^{-6}
$(D_{AM}/K\delta)_{NaCl}$, cm/s	1.790×10^{-5}	1.470×10^{-5}
X_{A2}		1.386×10^{-3}

For a membrane specified in terms of A and $D_{AM}/K\delta$, equations (12) and (13) enable one to predict membrane performance (solute separation and membrane flux) for any feed concentration X_{A1}, and any chosen feed flow condition specified in terms of k as follows. First determine, by trial and error, the particular combination of X_{A2} and X_{A3} which simultaneously satisfies equations (12) and (13), and also equation (10) when applicable. Using that combination of X_{A2} and X_{A3} values, determine N_B from equation (7). The above values of X_{A3} and N_B give the obtainable solute separation and membrane flux which may be expressed in terms of *f* and *PR* respectively as follows (ref. 1):

$$f = \frac{m_1 - m_3}{m_1} = 1 - \left\{\frac{X_{A3}}{1 - X_{A3}}\right\}\left\{\frac{1 - X_{A1}}{X_{A1}}\right\} \approx 1 - \frac{X_{A3}}{X_{A1}} \qquad (14)$$

$$PR = \frac{N_B \times M_B \times S \times 3600}{\left[1 - \dfrac{1}{\left\{1 + \dfrac{1000}{m_1(1 - f)M_A}\right\}}\right]} \qquad (15)$$

Using the above prediction procedure, one can calculate, for example, the effect of feed concentration and feed flow rate (as expressed by different values of k) on *f* and *PR* for a specified membrane.

A set of results of such calculations is illustrated in Figure 3 for the CA-398 and PPPH-8273 membranes specified in Table 7 with respect to NaCl-H_2O feed solutions in the solute concentration range 200 to 10,000 ppm.

These results also illustrate that while data on A and $(D_{AM}/K\delta)_{NaCl}$ (along with data needed for equation (10)) are enough to specify a membrane, they are not enough to predict membrane performance with respect to any solute, any feed concentration, and any feed flow rate; for such prediction, the relationship between $(D_{AM}/K\delta)_{NaCl}$ and $D_{AM}/K\delta$ for other solutes, and the applicable value of k are needed in addition to data on A and $(D_{AM}/K\delta)_{NaCl}$; variations in k can have significant effects on *f* and *PR*; and, consequently, reverse osmosis experimental or performance data on *f* and *PR* are always incomplete without the corresponding k value or its equivalent.

Considering the problem of predicting the reverse osmosis performance of a specified membrane at any point in the membrane-solution-operating system, the quantity A is independent of any solute under consideration, the quantity k is fixed either by choice or by operating conditions, or can be calculated from equation (11) or by other means (ref. 28), and hence the problem is primarily one of generating the applicable value of $D_{AM}/K\delta$ for the solute under consideration from data on $(D_{AM}/K\delta)_{NaCl}$ given in membrane specifications.

Relationships Between $(D_{AM}/K\delta)_{NaCl}$ and $D_{AM}/K\delta$ for Other Solutes

For completely ionized inorganic and (simple) organic solutes (refs. 12, 14, 15, 16),

$$(D_{AM}/K\delta)_{solute} \propto \exp\left\{n_c\left(-\frac{\Delta\Delta G}{RT}\right)_{cation} + n_a\left(-\frac{\Delta\Delta G}{RT}\right)_{anion}\right\} \qquad (16)$$

where n_c and n_a represent the number of moles of cation and anion respectively in one mole of ionized solute. Applying equation (16) to $(D_{AM}/K\delta)_{NaCl}$,

$$\ln(D_{AM}/K\delta)_{NaCl} = \ln C^*_{NaCl} + \left\{\left(-\frac{\Delta\Delta G}{RT}\right)_{Na^+} + \left(-\frac{\Delta\Delta G}{RT}\right)_{Cl^-}\right\} \qquad (17)$$

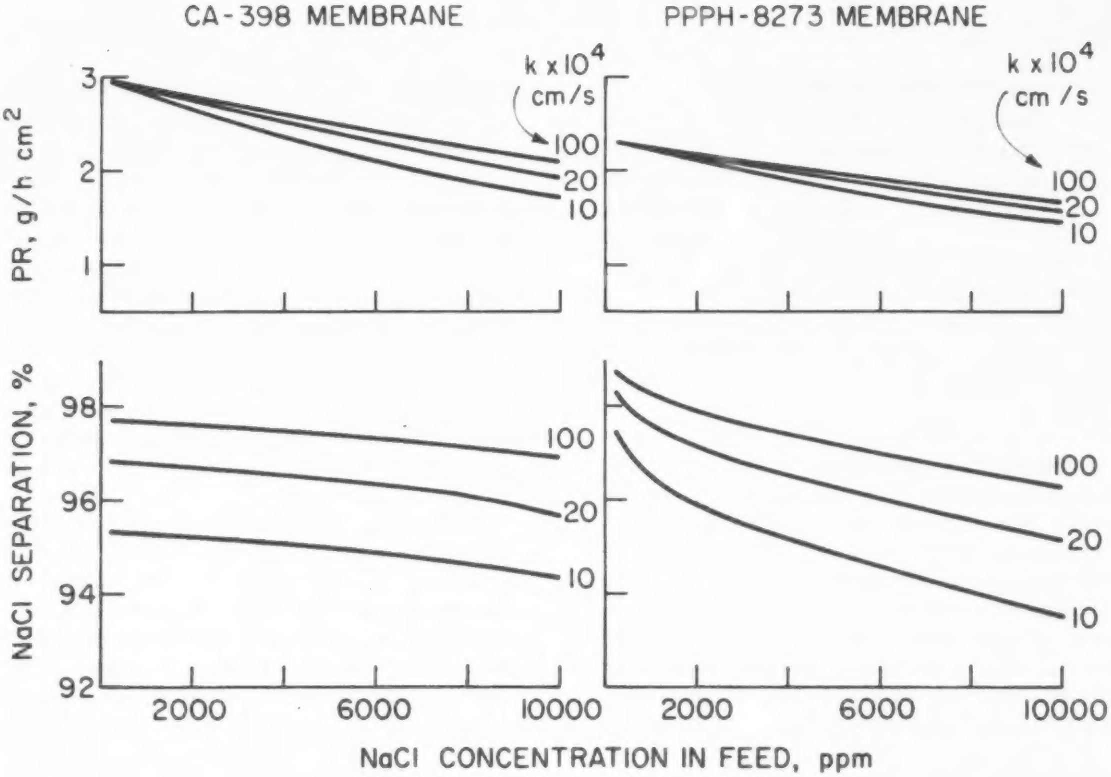


Figure 3. Effect of feed concentration and mass transfer coefficient k on the performance of the CA-398 and PPPH-8273 membranes specified in Table 7 for NaCl-H_2O feed solutions. Operating pressure = 405 psig.

where $\ln C^{*}_{NaCl}$ is a constant representing the porous structure of the membrane surface expressed in terms of $(D_{AM}/K\delta)_{NaCl}$. Using the data on $-\Delta\Delta G/RT$ for Na^{+} and Cl^{-} ions (Table 1) which are independent of $\ln C^{*}_{NaCl}$, the value of the latter can be calculated correspondingly to any given value of $(D_{AM}/K\delta)_{NaCl}$. Using the value of $\ln C^{*}_{NaCl}$ so obtained, the corresponding value for $D_{AM}/K\delta$ for any completely ionized inorganic or (simple) organic solute can be obtained from the relation

$$\ln(D_{AM}/K\delta)_{solute} = \ln C^{*}_{NaCl} + n_c\left\{\left(-\frac{\Delta\Delta G}{RT}\right)_{cation} + n_a\left(-\frac{\Delta\Delta G}{RT}\right)_{anion}\right\} . \quad (18)$$

Thus, for any specified value of $(D_{AM}/K\delta)_{NaCl}$, the corresponding values of $D_{AM}/K\delta$ for a large number of completely ionized solutes can be obtained from equation 18 using data on $-\Delta\Delta G/RT$ for different ions given in Table 1.

For the PPPH-8273 membrane considered for illustration in this work, $(D_{AM}/K\delta)_{NaCl}$ at $X_{A2} = 1.386 \times 10^{-3}$ was used to calculate $\ln C^{*}_{NaCl}$ for use in obtaining $(D_{AM}/K\delta)_{solute}$ values for nonionized organic solutes, and $(D_{AM}/K\delta)_{NaCl}$ at $X_{A2} = 0.830 \times 10^{-3}$ was used to calculate $\ln C^{*}_{NaCl}$ for use in obtaining $(D_{AM}/K\delta)_{solute}$ values for ionized inorganic solutes.

With respect to electrolytic inorganic solutes, a few special cases are of particular interest to water pollution control. Some solutes are subject to partial dissociation and ion-pair formation (for example, sulfates of divalent metals particularly at high concentrations) or partial hydrolysis (for example, Na_2CO_3, $FeCl_2$ etc.). For a solution system involving ions and ion pairs, equation (18) can be written as:

$$\ln(D_{AM}/K\delta)_{solute} = \ln C^*_{NaCl} + \alpha_D \left\{ n_c \left(-\frac{\Delta\Delta G}{RT}\right)_{cation} + n_a \left(-\frac{\Delta\Delta G}{RT}\right)_{anion} \right\} + (1-\alpha_D)\left\{-\frac{\Delta\Delta G}{RT}\right\}_{ip} \quad (19)$$

where α_D represents the degree of dissociation, and the subscript ip refers to the ion-pair formed; for the particular case where the ion-pair itself is an ion, equation (18) assumes the more general form

$$\ln(D_{AM}/K\delta)_{solute} = \ln C^*_{NaCl} + \alpha_D \left\{ n_c \left(-\frac{\Delta\Delta G}{RT}\right)_{cation} + n_a \left(-\frac{\Delta\Delta G}{RT}\right)_{anion} \right\} + (1-\alpha_D)\left(-\frac{\Delta\Delta G}{RT}\right)_{ip} + (1-\alpha_D)(n_c - n_{ipc})\left(-\frac{\Delta\Delta G}{RT}\right)_{cation} + (1-\alpha_D)(n_a - n_{ipc})\left(-\frac{\Delta\Delta G}{RT}\right)_{anion} \quad (20)$$

where the subscripts n_{ipc} and n_{ipa} are number of moles of cation and anion respectively involved in one mole of ion-pair. For example, when $K_3Fe(CN)_6$ dissociates to give K^+ and $Fe(CN)_6{}^{3-}$ ions, and the ion-pair $KFe(CN)_6{}^{2-}$, $n_c = 3$, $n_a = 1$, $n_{ipc} = 1$, and $n_{ipa} = 1$; when $K_4Fe(CN)_6$ dissociates to give K^+ and $Fe(CN)_6{}^{4-}$ ions, and the ion-pair $KFe(CN)_6{}^{3-}$, $n_c = 4$, $n_a = 1$, $n_{ipc} = 1$, and $n_{ipa} = 1$. Further, for the case of a feed solution which is subject to partial hydrolysis, equation (18) becomes

$$\ln(D_{AM}/K\delta)_{solute} = \ln C^*_{NaCl} + (1-\alpha_H)\left\{ n_c \left(-\frac{\Delta\Delta G}{RT}\right)_{cation} + n_a \left(-\frac{\Delta\Delta G}{RT}\right)_{anion} \right\} + \alpha_H \left\{ n_{hy} \left(-\frac{\Delta\Delta G}{RT}\right)_{hy} + \left(-\frac{\Delta\Delta G}{RT}\right)_{OH^- \text{ or } H^+} \right\} \quad (21)$$

where α_H represents the degree of hydrolysis, and the subscript hy refers to the hydrolyzed species resulting from the hydrolysis reaction and the subscripts OH^- and H^+ represent the hydroxyl and hydrogen ions respectively. In equations (19), (20), and (21), the applicable values of α_D and α_H are those corresponding to the boundary concentration X_{A2}.

Using equation (18) (and equation (19) when necessary) and data given in Table 1 for calculating the $D_{AM}/K\delta$ values for $MgCl_2$, Na_2SO_4, and $MgSO_4$ solutes, the corresponding data on solute separation and product rate were calculated at a constant value of $k (= 20 \times 10^{-4}$ cm/s) as a function of feed solution concentration (in the range 200 to 10,000 ppm of solute) for the CA-398 and PPPH-8273 membranes specified in Table 7. The results obtained are given in Figure 4, which illustrates the effect of chemical nature of solute and that of membrane material on reverse osmosis performance, and also the utility of equations (18) and (19) together with the basic transport equations (6) to (9) for predicting such performance data. The latter is further illustrated by data on solute separation presented in Appendix 1.

For a completely nonionized polar organic solute (refs. 13,27),

$$\ln(D_{AM}/K\delta)_{solute} = \ln C^*_{NaCl} + \ln \Delta^* + \left(-\frac{\Delta\Delta G}{RT}\right) + \delta^* \Sigma E_s + \omega^* \Sigma_s{}^* \,. \quad (22)$$

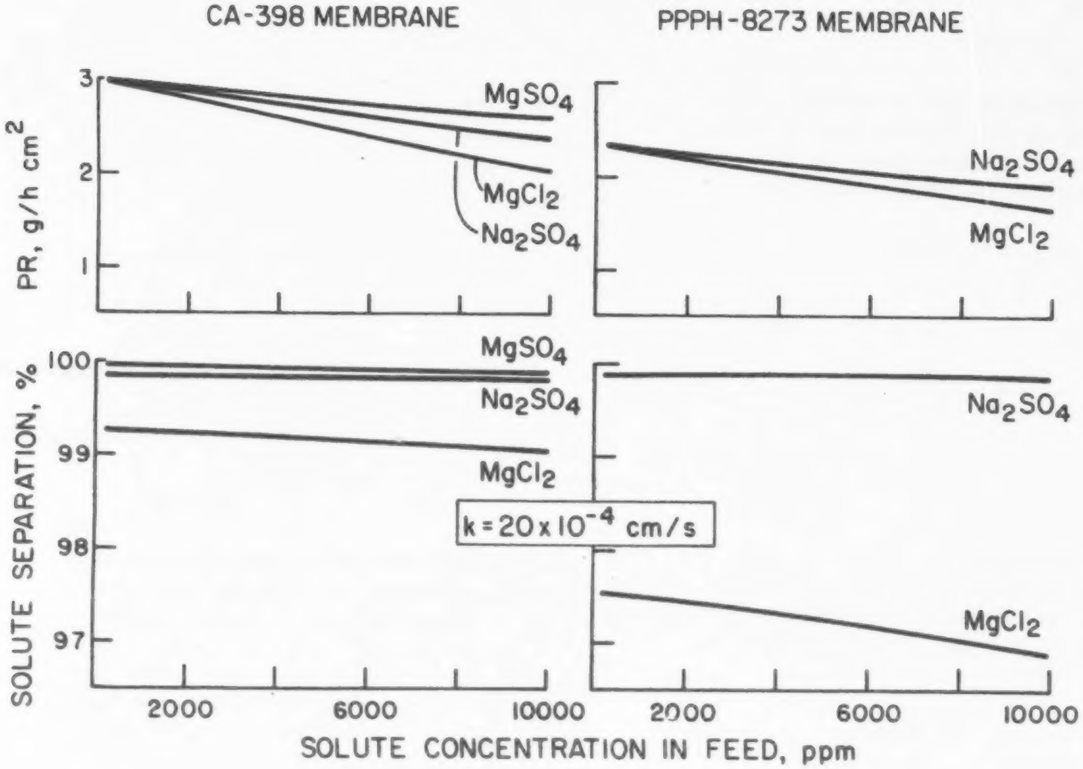


Figure 4. Effect of feed concentration on the performance of the CA-398 and PPPH-8273 membranes specified in Table 7 for aqueous feed solutions of different inorganic solutes. Operating pressure = 405 psig.

All quantities on the right side of equation (22), except ln Δ^*, have already been discussed. The quantity ln Δ^* sets a scale for ln $(D_{AM}/K\delta)_{solute}$ in terms of ln C^*_{NaCl} when the parameters representing the polar, steric, and nonpolar effects at the membrane-solution interface are each set equal to zero. Thus ln Δ^* is simply a scale factor, and it is a function of the chemical nature of the membrane material and the porous structure of the membrane surface. Experimental correlations of ln Δ^* vs. ln(C^*_{NaCl}/A) obtained for the CA-398 and PPPH-8273 membrane materials are given in Figure 5; these correlations are applicable for all nonionized polar organic solutes. Further, as stated already, as simply a matter of scale, the quantity $\omega^*\Sigma s^* = 0$ when the molecular structure of the polar organic solute involves no more than three carbon atoms not associated with a polar functional group. For practical calculations, equation (22) is used in conjunction with the data presented in Figures 1, 2, and 5, and Tables 2 to 6.

Transport Equations Applicable for Very Dilute Solutions

In the reverse osmosis treatment of many wastewaters, the latter can be treated as very dilute solutions if they satisfy the criteria that, in each case, the molar density of the solution is essentially that of pure water (i.e., $c_1 = c_2 = c_3 = c$), and the solute concentrations are sufficiently small so that the osmotic pressures involved in reverse osmosis are negligible compared to the operating pressure used, in which case $(PR) \approx (PWP)$. For such dilute feed solutions, the permeation velocity

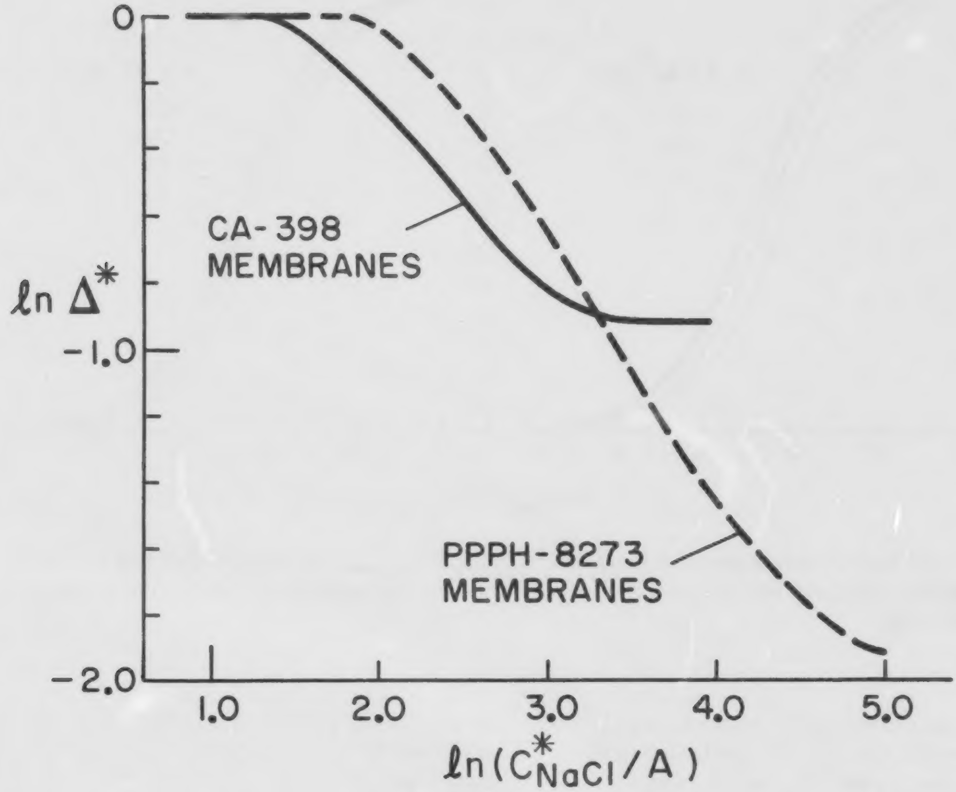


Figure 5. Correlation of ln Δ^* versus ln(C^*_{NaCl}/A) for CA-398 and PPPH-8273 membranes at 25° C.

(v_s) of the product solution through the membrane may be expressed as

$$v_s = \frac{AP}{c}\,. \tag{23}$$

Applying the basic transport equations (6) to (9) to such dilute feed solutions, $D_{AM}/K\delta$ for the solute involved can be expressed as (ref. 6):

$$(D_{AM}/K\delta)_{solute} = v_s\,\frac{(1-f)}{f}\left[\exp\left\{\frac{v_s}{k}\right\}\right]^{-1} \tag{24}$$

and hence

$$f = \left[1 + \frac{(D_{AM}/K\delta)_{solute}}{v_s}\,\exp\left\{\frac{v_s}{k}\right\}\right]^{-1}. \tag{25}$$

Equation (25) is an extremely useful relationship; it enables one to calculate solute separation *f* as a function of $(D_{AM}/K\delta)_{solute}$ for any given value of k for any specified membrane. The results of such calculations for the CA-398 and PPPH-8273 membranes specified in Table 7 are presented in Figure 6 as *f* vs. ln $(D_{AM}/K\delta)_{solute}$ for different k values. These correlations are applicable to both inorganic and organic solutes (whether ionized or nonionized) so long as the feed solution involved satisfies the criteria stated above for dilute solutions, and $(D_{AM}/K\delta)_{solute}$ is independent of X_{A2}. For such feed solution systems, one can calculate ln$(D_{AM}/K\delta)_{solute}$ for any solute from one of the applicable relations from the set of equations (18) to (22), and then directly read the corresponding solute separation *f* from Figure 6 for a wide range of k-values for the membranes specified in Table 7; thus the practical utility of the correlations of the type shown in Figure 6 is obvious.

In view of the practical importance of dilute feed solutions in the application of reverse

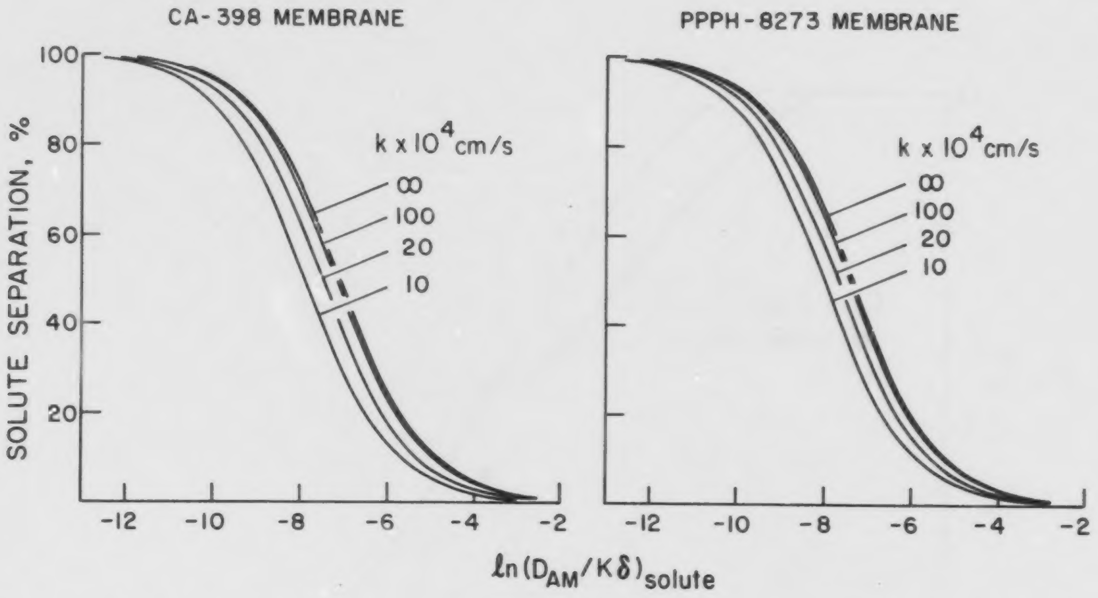


Figure 6. **Correlation of solute separation versus $\ln(D_{AM}/k\delta)_{solute}$ for the CA-398 and PPPH-8273 membranes specified in Table 7 for dilute aqueous feed solutions. Operating pressure = 405 psig.**

osmosis to water pollution control, solute separation data for the membranes specified in Table 7 were calculated for a large number of inorganic and organic solutes using the applicable relationships from the set of equations (18) to (25), and the physicochemical data given in Tables 1 to 6; the results obtained are given in Appendix 1.

The effect of operating pressure P on solute separation *f* is of interest in many water pollution control applications. According to equation (25), when the values of $(D_{AM}/K\delta)_{solute}$ and k remain constants and $v_s \propto P$ (which conditions are essentially satisfied in many reverse osmosis applications), then *f* tends to increase with increase in P for v_s/k values of <1, whereas *f* tends to decrease with increase in P for v_s/k values >1. These predictions of equation (25), which are both of fundamental and practical interest, have been experimentally verified (ref. 29).

Many polluted waters contain organic acids which are dissociated to different extents depending upon their concentrations. Reverse osmosis separations of such acids in dilute solutions can be calculated by determining separately the applicable $(D_{AM}/K\delta)$ value for the ionized part from equation (18), and that for the nonionized acid from equation (22), and then calculating solute flux N_A for each part separately from the general relation

$$N_A = (D_{AM}/K\delta)\, c\, (X_{A2} - X_{A3}). \qquad (26)$$

From the values of N_B (= AP) and total solute flux $(N_A)_{total}$ (= N_A for ionized part + N_A for nonionized acid), X_{A3} can be calculated from the relation

$$X_{A3} = (N_A)_{total} / \{N_B + (N_A)_{total}\} \qquad (27)$$

and then the solute separation *f* can be calculated from equation (14). Further computational details of this method of calculation are given in reference 14. Using this method, solute separation data for several organic acids were calculated as a function of feed concentration at a specified k value for the CA-398 membrane specified in Table 7, and the results obtained are given in Figure 7; additional data on *f* for a number of such organic acids are included in Appendix 1.

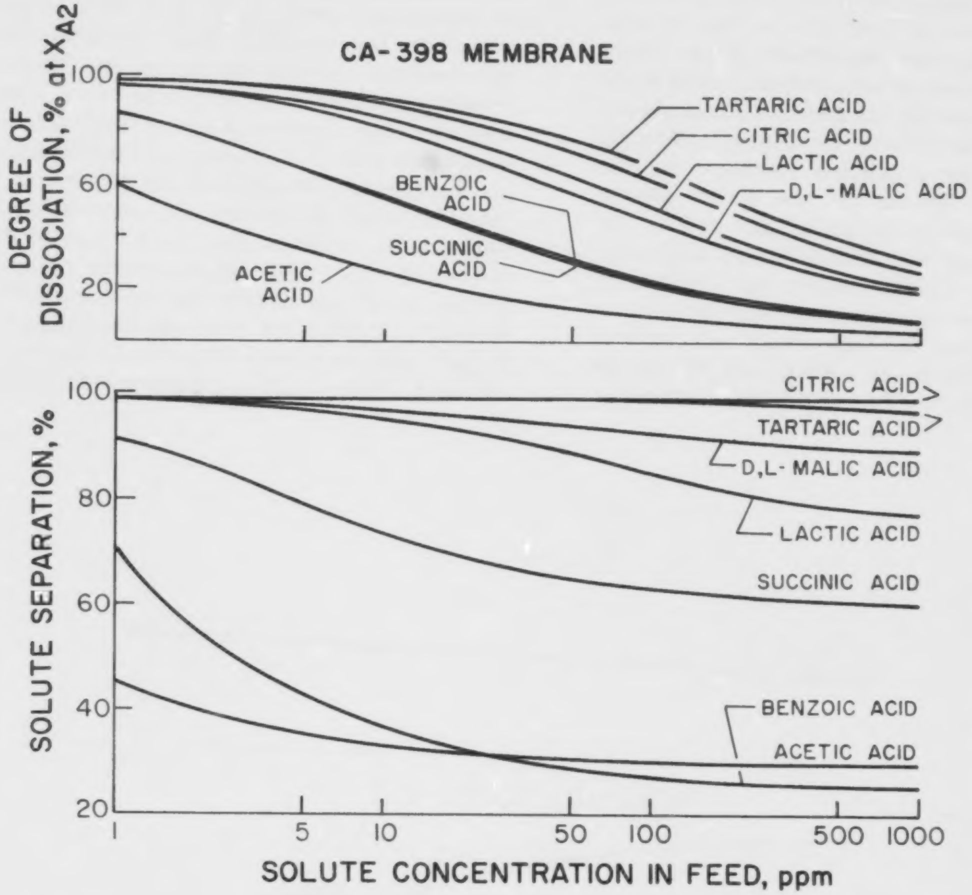


Figure 7. Effect of feed concentration on the performance of the CA-398 membrane specified in Table 7 for aqueous feed solutions of partially dissociated organic acids. Operating pressure = 405 psig; $k = 20 \times 10^{-4}$ cm/s.

Predictability of Membrane Performance for Aqueous Feed Solution Systems Involving Mixed-Solutes

The foregoing reverse osmosis transport equations refer specifically to single-solute aqueous feed solution systems. Most polluted waters, however contain more than one solute. Hence the predictability of membrane performance for feed solution systems involving mixed-solutes is of real interest in the application of reverse osmosis for water pollution control. Even though a comprehensive analytical technique for predicting such membrane performance in reverse osmosis for all kinds of mixed-solute systems from data on membrane specification only is yet to be developed, considerable progress has been made at least with respect to certain kinds of mixed-solute systems (refs. 1,18,30,31). The latter include (1) mixture of any number of electrolytic solutes involving a common ion (ref. 1), (2) mixture of any number of nonionized organic solutes with no mutual solute-solute interactions (refs. 18, 30) and (3) mixture of two uni-univalent electrolytic solutes without a common ion (ref. 31). The techniques involved for predicting membrane performance (i.e., both solute separation and rate of membrane permeated product) for the above kinds of mixed-solute systems are described fully in the indicated references. Briefly, the techniques involved for the mixed-solute systems (1) and (2) use the reverse osmosis transport equations given above treating each solute independently, so that the net result is simply the additive effect of each individual component in the mixed-solute system. In the prediction technique for the mixed-solute system (3), the basic reverse osmosis transport equations are written for each ion along with the necessary additional equations for overall electroneutrality for the system; these equations together with equation (18) written for each possible electrolytic solute combining the cations and the anions present in the system, yield a set of equations which can be solved to give the necessary data on ion separations and product rates from data on membrane specifications only. This latter technique has recently been extended to mixed-solute systems involving one monovalent-monovalent electrolyte and one divalent-monovalent electrolyte (ref. 32). These techniques (refs. 31, 32) are simple in principle and fundamental in approach but require considerable effort in solving the computational complexities involved. For the purpose of illustration, the mixed solute system sodium acetate + calcium nitrate was analyzed with respect to the CA-398 membrane specified in Table 7, and the results obtained are shown in Figure 8. These results are significant from the

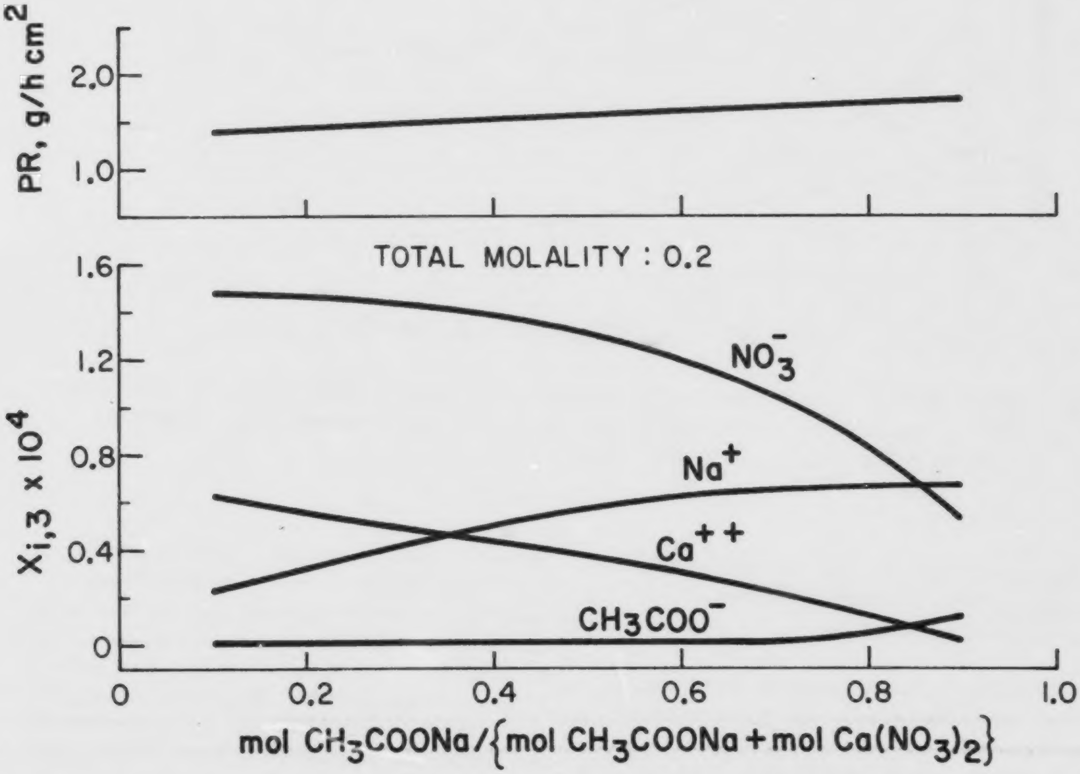


Figure 8. Effect of relative concentration of CH_3COONa on ion flux and product rate for 0.2 molal feed solution CH_3COONa-$Ca(NO_3)_2$-H_2O during reverse osmosis operation using the CA-398 membrane specified in Table 7. Operating pressure = 405 psig; $k_{NaCl} = 20 \times 10^{-4}$ cm/s.

points of view of both water pollution control and fractionation of dissolved solutes by reverse osmosis.

Predictability of Performance of Commercial Reverse Osmosis Modules

The basic transport equations given above (equations (6) to (9)) apply to any point in the reverse osmosis system. With reference to commercial reverse osmosis modules, this means that solute separation and product rate values predicted by the above equations correspond to values obtainable at module entrance or at zero product water recovery. The true performance of an entire module, however, involves a finite fraction recovery (Δ) of product water whose concentration changes continuously from the entrance end to the exit end of the module. Thus the module as a whole has an average solute separation ($\bar{f}$) and an average product rate. This performance of the module as a whole can be predicted by applying the basic transport equations to the entire reverse osmosis system and analyzing the various relationships applicable to the system. Such system analysis is simple in principle, fundamental in approach, and often complex in computation. The technique for such analysis has been developed in detail with particular reference to water treatment applications and CA-398 membranes (refs. 33,34). The following is a brief outline of this technique.

System Specification

Any reverse osmosis system may be specified in terms of three nondimensional parameters γ, θ, and λ defined as:

$$\gamma = \frac{\pi(X^{o}_{A1})}{P} = \frac{\text{osmotic pressure of initial feed solution}}{\text{operating pressure}}, \tag{28}$$

$$\theta = \frac{(D_{AM}/K\delta)}{v^{*}_{w}} = \frac{\text{solute transport parameter}}{\text{pure water permeation velocity}}, \text{ and} \tag{29}$$

$$\lambda = \frac{k}{(D_{AM}/K\delta)} = \frac{\text{mass transfer coefficient on the high pressure side of membrane}}{\text{solute transport parameter}} \tag{30}$$

The quantity v^{*}_{w} is obtained from the relation

$$v^{*}_{w} = \frac{AP}{c} \tag{31}$$

and the quantity $\pi(X^{o}_{A1})$ refers to the osmotic pressure of the feed solution at membrane entrance in a flow process or start of operation in a batch process. The quantities γ, θ, and $\lambda\theta\,(= k/v^{*}_{w})$ may be described as the osmotic pressure characteristic, membrane characteristic, and the mass transfer coefficient characteristic respectively for the reverse osmosis system under consideration. The significance of system specification is that a single set of numerical parameters can represent an infinite number of membrane-solution-operating systems; conversely, any two membrane-solution-operating systems can be simply and precisely differentiated in terms of unique combinations of numerical parameters.

System Analysis

Figure 9 indicates the performance parameters of a reverse osmosis system. The dimensionless concentration C is defined in terms of actual concentration ratios as

$$C = X_{A}/X^{o}_{A1} \tag{32}$$

so that

$$C_{1} = X_{A1}/X^{o}_{A1} \tag{33}$$

$$C^{o}_{1} = X^{o}_{A1}/X^{o}_{A1} = 1 \tag{34}$$

$$C_{2} = X_{A2}/X^{o}_{A1} \tag{35}$$

$$C^{o}_{2} = X^{o}_{A2}/X^{o}_{A1} \tag{36}$$

$$C_{3} = X_{A3}/X^{o}_{A1} \tag{37}$$

$$C^{o}_{3} = X^{o}_{A3}/X^{o}_{A1} \tag{38}$$

$$\overline{C}_{3} = \overline{X}_{A3}/X^{o}_{A1}. \tag{39}$$

Thus the quantities C_1, C_2, and C_3 represent the concentrations of the bulk solution and the concentrated boundary solution on the high pressure side of the membrane and the membrane permeated product solution on the low pressure side of the membrane respectively at any point in the system; the quantities C_1^o, C_2^o, and C_3^o are the values of C_1, C_2, and C_3 respectively at membrane entrance in flow process, or at start of operation in batch process; and, the quantity $\overline{C}_3$ is the average value of C_3 corresponding to a specified fraction Δ of product water recovery. Further, a dimensionless longitudinal length parameter X for a flow process, and a dimensionless time parameter τ for a batch process are defined as:

$$X = \frac{v_w^*}{\overline{u}^o} \frac{x}{h} \tag{40}$$

and

$$\tau = \frac{S\, v_w^*\, t}{V_1^o} . \tag{41}$$

When $(1/h) \equiv (S/V_1^o)$, and $(x/\overline{u}^o) \equiv t$, the numerical values of X and τ are identical. The quantities C_1, C_2, C_3, $\overline{C}_3$, τ or X, and Δ represent the main performance data for any specified reverse osmosis system.

On the basis of the transport equations (6) to (9), and the foregoing definitions, and a few reasonable assumptions applicable for most water treatment applications of reverse osmosis, it has been shown that in any reverse osmosis system specified in terms of γ, θ, and λ, the quantities v_w(= local permeation velocity of product water) and v_w^*, C_2 and C_3, C_1 and C_3, C_1 and $\overline{C}_3$, C_3 and τ or X, and C_3 and Δ are uniquely related as follows:

$$v_w = v_w^* \left[1 - \gamma(C_2 - C_3)\right] \tag{42}$$

$$C_2 = C_3 \left[1 + \frac{1}{(\gamma C_3 + \theta)}\right] \tag{43}$$

$$C_2^o = C_3^o \left[1 + \frac{1}{(\gamma C_3^o + \theta)}\right] \tag{44}$$

$$C_1 = C_3 \left[1 + \frac{1}{(\gamma C_3 + \theta)} \exp \left\{- \frac{1}{\lambda(\gamma C_3 + \theta)}\right\}\right] \tag{45}$$

$$C_1^o = 1 = C_3^o \left[1 + \frac{1}{(\gamma C_3^o + \theta)} \exp \left\{- \frac{1}{\lambda(\gamma C_3^o + \theta)}\right\}\right] \tag{46}$$

$$C_1(1 - \Delta) + \overline{C}_3 \Delta = 1 \tag{47}$$

$$\Delta = 1 - \exp(-Z) \tag{48}$$

$$\text{where } Z = \int_{C_3^o}^{C_3} \left[\frac{\gamma}{\lambda(\gamma C_3 + \theta)^2} - \frac{\gamma}{(\gamma C_3 + \theta)} + \left\{\frac{(\gamma C_3 + \theta)}{C_3} \exp \frac{1}{\lambda(\gamma C_3 + \theta)}\right\} + \frac{1}{C_3} \right] dC_3 \tag{49}$$

and

$$\left\{\begin{matrix}\tau \\ \text{or} \\ X\end{matrix}\right\} = \int_{C_3^o}^{C_3} \left[\frac{\gamma}{\lambda(\gamma C_3 + \theta)} - \gamma + \frac{(\gamma C_3 + \theta)}{C_3} \left\{1 + (\gamma C_3 + \theta) \exp \frac{1}{\lambda(\gamma C_3 + \theta)}\right\}\right] \frac{\exp(-Z)}{\theta}\, dC_3 \tag{50}$$

The above relationships show that with respect to a specified reverse osmosis system, if any 4 of the 12 quantities of γ, θ, λ (or $\lambda\theta$), Z, Δ, C_1, C_2, C_2^o, C_3, C_3^o, $\overline{C}_3$, τ or X are fixed, the remaining 8 quantities can be obtained by simultaneous solution of equations (42) to (50).

Illustrative Calculations

A commercial ROGA-4000 reverse osmosis module with a cellulose acetate (assumed to be CA-398) membrane has the following dimen-

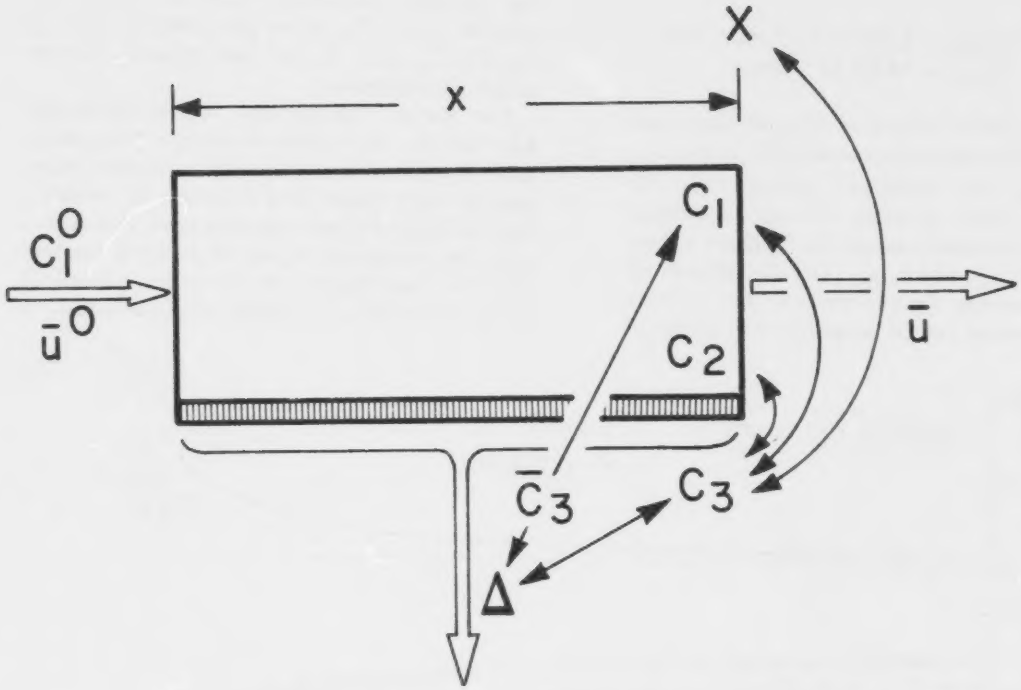


Figure 9. Performance parameters for a reverse osmosis system.

sional characteristics:

effective area of film surface = 5.763×10^4 cm^2,
longitudinal length for feed flow, x = 73.7 cm,
membrane area per unit volume of fluid space, h^{-1} = 18.19 cm^{-1}, and
cross sectional area of module = 44.15 cm^2.

A single reverse osmosis experiment with the above module gave the following data for a 3,500 ppm NaCl-H_2O reference feed solution whose osmotic pressure is 40 psi:

operating pressure = 400 psig
pure water permeation rate = 0.75 gal/min
feed flow rate at module entrance = 3.45 gal/min
product rate = 0.656 gal/min
flow rate of concentrate = 2.794 gal/min
concentration of NaCl in product = 140 ppm.

From the above data, the values for the four quantities γ, Δ, $\bar{C}_3$, and X can be calculated to be as follows:

γ = π(3,500 ppm NaCl)/400 = 0.1
Δ = product rate/feed flow rate = 0.19
$\bar{C}_3$ = NaCl concentration in product/NaCl concentration in feed = 0.04
v_w^* = pure water permeation rate/effective area of film surface = 8.242×10^{-4} cm/s
$\bar{u}^0$ = feed flow rate/cross sectional area of module = 4.95 cm/s
X = $v_w^* \; x/\bar{u}^0 h$ = 0.2232.

Solving equations (42) to (50) simultaneously, the values of θ and $\lambda\theta$ corresponding to the above values of γ, Δ, $\bar{C}_3$, and X are obtained as

$$\theta = 0.02176, \text{ and}$$
$$\lambda\theta = 2.233$$

from which the values of $(D_{AM}/K\delta)_{NaCl}$ for the membrane in the module and k_{NaCl} for the operating conditions of the module can be calculated to be

$$(D_{AM}/K\delta)_{NaCl} = 1.793 \times 10^{-5} \text{ cm/s, and}$$
$$k_{NaCl} = 18.4 \times 10^{-4} \text{ cm/s.}$$

From the above values of $(D_{AM}/K\delta)_{NaCl}$ and k_{NaCl}, the corresponding values of $(D_{AM}/K\delta)_{solute}$ and k_{solute} for different solutes can be calculated using equation (11) and equations (18) to (22) discussed earlier. Using these values of $(D_{AM}/K\delta)_{solute}$ and k_{solute}, and the value of v_w^* obtained already for the module, the reverse osmosis system can be respecified in terms of γ, θ, and λ for any desired feed solution system. These latter three parameters, together with the already calculated value of X for the module, yield the other performance data Δ, C_1, C_2, C_3, and $\overline{C}_3$ for the solution system under consideration.

For further illustration, a few numerical data for the above ROGA module were calculated by system analysis with particular reference to very dilute feed solutions for which γ may be assumed to be equal to zero. For such a case, the numerical values of Δ and X become identical, and Figure 10 shows the effects of variations of (1) k_{NaCl} and (2) nature of solute on

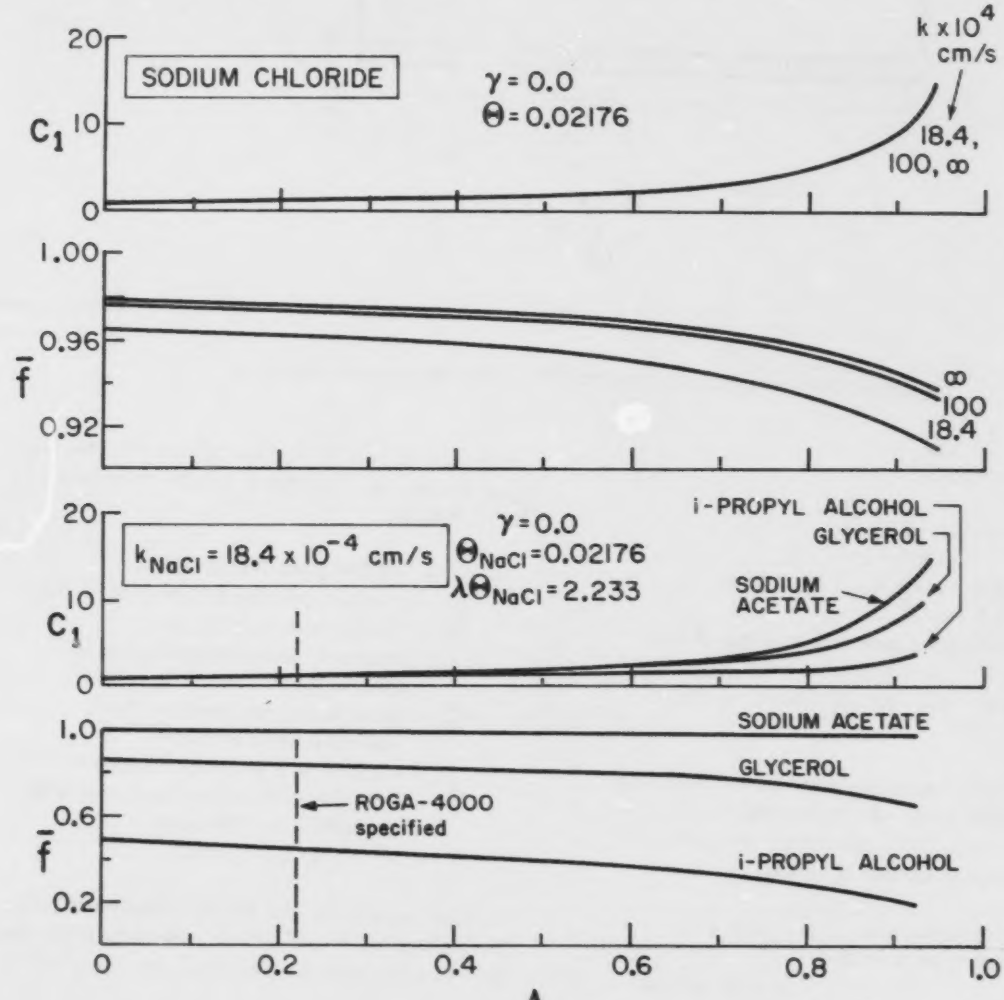


Figure 10. Some results of system analysis for a reverse osmosis module for very dilute feed solutions.

average solute separation $\bar{f}(=1-\bar{C}_3)$, and the ratio, solute concentration in the concentrate leaving the system/solute concentration in the feed entering the system = C_1, as a function of fraction product water recovery. For the particular ROGA module analyzed, when $\gamma = 0$, $\theta = 0.02176$ and $\lambda\theta = 2.233$, $\Delta = 0.2232$; the values of $\bar{f}$ and C_1 corresponding to this value of Δ are indicated in Figure 10 by dotted lines.

The foregoing calculations illustrate the application of basic transport equations and system analysis for predicting the performance of reverse osmosis membranes and modules; conversely, one can also perform similar calculations to specify the membranes and modules needed to obtain a given reverse osmosis performance.

A FUNDAMENTAL APPROACH TO SOME OF THE OTHER ASPECTS OF REVERSE OSMOSIS RELEVANT TO WATER POLLUTION CONTROL

Preferential Sorption of Solute at Membrane-Solution Interfaces

The transport equations and predictability techniques discussed above apply specifically to reverse osmosis systems where water is preferentially sorbed at the membrane-solution interface. There are a large number of practically important reverse osmosis systems where solute is preferentially sorbed at the interface. For example, with respect to cellulose acetate membranes and aqueous solutions, such systems involve solutes such as phenols, chlorinated and/or aromatic hydrocarbons, mineral oils, higher alcohols, and many undissociated organic compounds. For such reverse osmosis systems, comprehensive precise criteria for preferential sorption of solute at membrane-solution interface, and transport equations and predictability techniques similar to those described above are yet to be fully developed. However, certain characteristics of such systems are known (refs. 26,35,36,37). When solute is preferentially sorbed at the membrane-solution interface, solute separation in reverse osmosis can be positive, negative, or zero, depending on the nature of solute, membrane, and experimental conditions; under otherwise identical experimental conditions, solute separation can pass through a maximum and minimum with decrease in average pore size on the membrane surface, and solute separation generally decreases with increase in operating pressure. Solute preferential sorption results in pore-blocking effect, so that even when the osmotic pressure effects involved are negligible, the *PR/PWP* ratio is significantly less than unity. The quantities 1-(*PR/PWP*) (which is a measure of pore-blocking effect) and N_A (solute flux) are both unique functions of X_{A2} for the calculation of which equation (9) is still applicable.

Temperature Effects

The effects of operating temperature on (1) A, $(D_{AM}/K\delta)_{solute}$, and k_{solute}, (2) the rate of any chemical reactions involved (such as hydrolysis, dissociation, etc.), and (3) the physical properties of the membrane (compaction, swelling, etc.), and the result of such effects on the overall performance of the reverse osmosis system are all yet to be studied in detail.

Effects of pH

The pH of the feed solution may change the chemical nature of the solute species and/or that of the membrane surface due to dissociation and/or hydrolysis reactions. Such changes must naturally affect the performance of the membrane during reverse osmosis. The effects of such changes must be distinguished from the effects of other parameters governing reverse osmosis separations in the choice of appropriate reverse osmosis systems for specific applications.

Membrane Compaction

The factors governing membrane compaction in reverse osmosis include (1) molecular structure and physical properties of the membrane material, (2) overall porous structure of the membrane arising from specific membrane making conditions, and (3) reverse osmosis experimental conditions. Precise quantitative relationships between membrane compaction and the above factors have not yet been studied in detail.

Membrane Fouling

The term "fouling" represents no definite scientific phenomenon; it is just an incoherent description of the occurrence of flux decline of product water during reverse osmosis due to a variety of reasons which include (1) pore-blocking by suspended or colloidal matter present in the feed solution, (2) pore-blocking due to precipitation of some solid from the feed solution during reverse osmosis, (3) pore-blocking due to solute preferential sorption at the membrane-solution interface, (4) high concentration polarization on the high pressure side of the membrane, (5) low solute diffusivity and low mass transfer coefficient on the high pressure side of the membrane, (6) high viscosity of the boundary solution on the high pressure side of the membrane, (7) pre-gel or gel formation on the high pressure side of the membrane, (8) membrane compaction, and (9) chemical and physicochemical processes affecting the chemical nature and porous structure of the membrane. Often several of the above reasons contribute simultaneously to flux decline during reverse osmosis. Therefore practical solutions to the problem of membrane fouling must be based on an understanding of the causes of such fouling in the particular reverse osmosis application concerned.

Ultrafiltration (UF) and Reverse Osmosis (RO)

The distinction between UF and RO is not well defined, and it will continue to be so because of historical and practical reasons. This need not prevent a basic understanding of these two processes which are extremely important for water pollution control applications. Simply because the osmotic pressure of the solution involved is low or negligible, or the molecular weight of the solute involved is high, or the operating pressure for the system is low, or the resulting water flux in the system is high, the process involved does not become UF nor does it cease to be RO. If UF is restricted to size separation by mechanical sieve filtration, and RO is restricted to solute separation by virtue of preferential sorption of solvent or solute at the membrane-solution interface, the two processes are mutually exclusive and can be treated as such, even though both processes may occur simultaneously in a given system. Further, even when the process involved is clearly a mechanical sieving operation, the chemical nature and porous structure of the membrane surface may have significant effects on the filtration characteristics of the system. These considerations point to the need for a critical study of the UF and RO processes involved in practical membrane separation systems nominally described as ultrafiltration.

CONCLUSION

The field of reverse osmosis is new, open, visible, and versatile. In the present context of widespread industrial pollution and public concern on the quality of our environment, the effective utilization of reverse osmosis for water pollution control would make the social relevance of reverse osmosis second to none. For such utilization, one must understand and develop the science of reverse osmosis. The physicochemical basis for reverse osmosis separations, the materials science of reverse osmosis membranes, and the engineering science of reverse osmosis transport are the major components of the science of reverse osmosis. All applications of reverse osmosis arise from this science. The development and practical utilization of this science calls for dedicated efforts. This paper is part of such efforts.

REFERENCES

1. S. Sourirajan, *Reverse Osmosis*, Chapters 1, 2, 3, and 6, and Appendix 1, Academic Press, New York, 1970.
2. *Reverse Osmosis and Synthetic Membranes*, S. Sourirajan, ed., National Research Council Canada, Ottawa, 1977.
3. S. Sourirajan, *Pure Appl. Chem.*, Vol. 50, No. 7, p. 593, 1978.
4. S. Sourirajan, *Reverse Osmosis and Synthetic Membranes*, S. Sourirajan, ed., Chap. 1, National Research Council Canada, Ottawa, 1977.
5. S. Sourirajan, *Ind. Eng. Chem. Fundamentals*, Vol. 2, p. 51, 1963.
6. S. Sourirajan and T. Matsuura, *Reverse Osmosis and Synthetic Membranes*, S.

Sourirajan, ed., Chapters 2 and 3, National Research Council Canada, Ottawa, 1977.

7. L. E. Applegate and C. R. Antonson, *Reverse Osmosis Membrane Research,* H. K. Lonsdale and H. E. Podall, eds., p. 243 Plenum, New York, 1972.
8. T. Matsuura, P. Blais, L. Pageau, and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 16, p. 510, 1977.
9. T. Matsuura, P. Blais, and S. Sourirajan, *J. Appl. Polym. Sci.*, Vol. 20, p. 1515, 1976.
10. T. Matsuura and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 17, p. 419, 1978.
11. S. Sourirajan and B. Kunst, *Reverse Osmosis and Synthetic Membranes,* S. Sourirajan, ed., Chapter 7, National Research Council Canada, Ottawa, 1977.
12. T. Matsuura, L. Pageau, and S. Sourirajan, *J. Appl. Polym. Sci.*, Vol. 19, p. 179, 1975.
13. T. Matsuura, J. M. Dickson, and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 15, p. 149, 1976.
14. T. Matsuura, J. M. Dickson, and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 15, p. 350, 1976.
15. R. Rangarajan, T. Matsuura, E. C. Goodhue, and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 15, p. 529, 1976.
16. R. Rangarajan, T. Matsuura, E. C. Goodhue, and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 17, p. 71, 1978.
17. R. W. Taft, Jr., *Steric Effects in Organic Chemistry,* M. S. Newman, ed., pp. 556-675, Wiley, New York, 1956.
18. T. Matsuura, M. E. Bednas, and S. Sourirajan, *J. Appl. Polym. Sci.*, Vol. 18, p. 567, 1974.
19. T. Matsuura, M. E. Bednas, J. M. Dickson, and S. Sourirajan, *J. Appl. Polym. Sci.*, Vol. 18, p. 2829, 1974.
20. T. Matsuura, M. E. Bednas, J. M. Dickson, and S. Sourirajan, *J. Appl. Polym. Sci.*, Vol. 19, p. 2473, 1975.
21. L. G. Sillen and A. E. Martell, "Stability Constants of Metal Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.
22. C. P. Bean, *Research and Development Progress Report,* No. 465, OSW, U.S. Dept. Interior, Washington, DC, 1969.
23. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, Vol. 18, p. 3593, 1974.
24. E. N. Pereira, T. Matsuura, and S. Sourirajan, *J. Food Sci.*, Vol. 41, p. 672, 1976.
25. P. A. Small, *J. Appl. Chem.*, Vol. 3, p. 71, 1953.
26. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, Vol. 17, p. 3683, 1973.
27. T. Matsuura, A. G. Baxter, and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 16, p. 82, 1977.
28. S. Kimura and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 7, p. 539, 1968.
29. F. Hsieh, T. Matsuura, and S. Sourirajan, *J. Appl. Polym. Sci.*, in press.
30. T. Matsuura and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 10, p. 102, 1971.
31. R. Rangarajan, T. Matsuura, E. C. Goodhue, and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 17, p. 46, 1978.
32. R. Rangarajan, T. Matsuura, E. C. Goodhue, and S. Sourirajan, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 23, p. 561, 1979.
33. H. Ohya and S. Sourirajan, *Reverse Osmosis System Specification and Performance Data for Water Treatment Applications,* The Thayer School of Engineering, Dartmouth College, Hanover, NH, 1971.
34. S. Sourirajan and H. Ohya, *Reverse Osmosis and Synthetic Membranes,* S. Sourirajan, ed., Chapter 4, National Research Council Canada, Ottawa, 1977.
35. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, Vol. 16, p. 2531, 1972.
36. T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, Vol. 17, p. 3661, 1973.
37. J. M. Dickson, T. Matsuura, and S. Sourirajan, "Transport Characteristics in the Reverse Osmosis System p-Chlorophenol-Water-Cellulose Acetate Membrane," *Ind. Eng. Chem. Process Des. Dev.*, in press.

APPENDIX 1.

(a) CALCULATED DATA ON REVERSE OSMOSIS SEPARATIONS OF DIFFERENT SOLUTES FOR THE CA-398 MEMBRANE SPECIFIED IN TABLE 7

Operating conditions: very dilute feed solutions; Operating pressure: 405 psig; $k_{NaCl} = 20 \times 10^{-4}$ cm/s

Solute	$k \times 10^4$ cm/s	Sepn. %
NaCl	20	96.8
Inorganic solutes		
$Al(NO_3)_3$	14.5	99.5
NH_4Br	23.3	95.8
NH_4Cl	23.0	96.4
NH_4I	23.1	94.5
NH_4NO_3	22.5	92.6
$BaBr_2$	18.3	99.1
$BaCl_2$	18.2	99.4
BaI_2	18.2	98.5
$Ba(NO_3)_2$	17.7	97.2
$Cd(NO_3)_2$	17.2	96.5
$CdSO_4^*$	13.1	>99.9
$CaBr_2$	17.8	98.7
$CaCl_2$	17.6	99.1
CaI_2	17.7	97.8
$Ca(NO_3)_2$	17.2	95.9
$Ce(NO_3)_2$	16.9	99.4
CsBr	23.6	96.7
CsCl	23.5	97.2
CsI	23.5	95.7
$CsNO_3$	22.9	94.2
$Cr(NO_3)_3$	16.7	98.8
$Co(NO_3)_2$	16.8	96.3
$CoSO_4^*$	12.6	>99.9
$Cu(NO_3)_2$	16.6	97.4
$CuSO_4^*$	17.1	99.1
$FeCl_2$	16.9	98.6
$Fe(NO_3)_2$	16.7	93.7
$Fe(NO_3)_3$	15.4	99.7
$LaCl_3$	17.3	99.4
$La(NO_3)_3$	16.7	94.3
$Pb(NO_3)_2$	18.3	97.5
LiBr	18.0	96.2
LiCl	17.9	96.7
LiF	16.5	97.9
LiI	18.0	95.0
$LiNO_3$	17.6	93.2
$MgBr_2$	17.0	98.9
$MgCl_2$	16.9	99.2
MgI_2	16.9	98.1
$Mg(NO_3)_2$	16.5	96.5
$MgSO_4^*$	13.0	>99.9
$Mn(NO_3)_2$	16.6	96.9
$MnSO_4^*$	13.1	>99.9
$Ni(NO_3)_2$	16.6	97.2
$NiSO_4^*$	13.1	>99.9
K acetate	18.2	99.2
K anisate	15.6	98.9
K benzoate	16.4	98.8
KBr	23.3	96.0
$KBrO_3$	20.6	97.8
K butyrate	16.8	99.2
K o-chlorobenzoate	16.5	99.5
K p-chlorobenzoate	16.4	98.8
KCl	23.0	96.6
$KClO_3$	21.7	95.3
$KClO_4$	22.1	92.5
$K_2CO_3^*$	18.5	>99.9
$K_2C_2O_4$	11.7	99.9
K_2CrO_4	19.5	99.9
$K_2Cr_2O_7$	16.7	98.3
K cyclohexylcarboxylate	16.3	99.4
KF	20.6	97.8
KHCOO	20.5	97.5
$KHCO_3$	18.9	98.5
KH phthalate	20.1	97.1
KH_2PO_4	18.0	99.3
$KHSO_4$	19.8	99.4
K hydroxybenzoate	16.4	98.8
KI	23.1	94.8
KIO_3	18.2	98.9
$K_3Fe(CN)_6^*$	19.0	>99.9
$K_4Fe(CN)_6^*$	18.8	>99.9
K isobutyrate	16.8	99.3
K m-nitrobenzoate	16.5	99.1
K o-nitrobenzoate	16.5	99.6
K p-nitrobenzoate	16.5	99.1
KNO_2	20.9	94.0

(continued)

APPENDIX 1 (continued).

Solute	$k \times 10^4$ cm/s	Sepn. %
KNO_3	22.5	93.0
KOH	29.3	99.4
K phenylacetate	16.0	98.8
K 4-phenylbutyrate	14.2	99.0
K β-phenylpropionate	14.5	99.0
K pivalate	16.3	99.7
K propionate	17.0	99.3
K_2SO_3	18.7	99.8
K_2SO_4	19.4	99.8
$K_2S_2O_3$	19.7	>99.9
K toluate	16.4	98.9
K valerate	16.6	99.3
RbBr	23.7	96.2
RbCl	23.5	96.8
RbI	23.5	95.1
$RbNO_3$	23.0	93.3
Na acetate	16.5	99.2
Na anisate	14.4	99.0
Na benzoate	15.0	98.9
NaBr	20.1	96.3
$NaBrO_3$	18.3	97.9
Na butyrate	15.4	99.3
Na o-chlorobenzoate	15.1	99.5
Na p-chlorobenzoate	15.0	98.9
$NaClO_3$	19.1	95.6
$NaClO_4$	19.3	93.0
Na_2CO_3*	16.1	>99.9
$Na_2C_2O_4$	10.9	99.9
Na_2CrO_4	16.9	99.9
$Na_2Cr_2O_7$	14.8	98.6
Na cyclohexylcarboxylate	14.9	99.4
NaF	18.3	98.0
NaHCOO	18.2	97.7
$NaHCO_3$	16.9	98.6
NaH phthalate	17.9	97.3
NaH_2PO_4	16.3	99.4
$NaHSO_4$	17.8	99.4
Na hydroxy-benzoate	15.0	98.9
NaI	20.0	95.2
$NaIO_3$	16.4	99.0
$Na_3Fe(CN)_6$*	16.3	>99.9
$Na_4Fe(CN)_6$*	16.0	>99.9
Na isobutyrate	15.4	99.3
Na m-nitrobenzoate	15.0	99.2

Solute	$N10^4$ cm/s	Sepn. %
Na o-nitrobenzoate	15.0	99.6
Na p-nitrobenzoate	15.0	99.2
$NaNO_2$	18.5	94.4
$NaNO_3$	19.6	93.5
NaOH	15.1	99.4
Na phenylacetate	14.6	98.9
Na 4-phenylbutyrate	13.2	99.1
Na β-phenylpropionate	13.5	99.1
Na pivalate	14.9	99.7
Na propionate	15.5	99.3
Na_2SO_3	16.6	99.8
Na_2SO_4	16.7	99.8
$Na_2S_2O_3$	17.1	>99.9
Na toluate	12.0	98.8
Na valerate	15.2	99.3
$SrBr_2$	17.8	98.9
$SrCl_2$	17.6	99.2
SrI_2	17.7	98.1
$Sr(NO_3)_2$	17.3	96.4
$Th(NO_3)_4$	11.1	99.9
$Zn(NO_3)_2$	16.5	96.3
$ZnSO_4$*	13.0	>99.9
Alcohols		
Methanol	22.6	9.4
Ethanol	18.7	18.2
1-Propanol	16.5	29.3
2-Propanol	16.5	48.0
1-Butanol	15.0	21.8
2-Butanol	15.0	49.7
2-Methyl-1-propanol	15.0	49.7
2-Methyl-2-propanol	15.0	86.8
1-Pentanol	13.9	18.5
2-Pentanol	13.9	51.7
3-Pentanol	13.9	51.7
2-Methyl-1-butanol	13.9	51.7
3-Methyl-1-butanol	13.9	51.7
2,2-Dimethyl-1-propanol	13.9	75.7
1-Hexanol	13.0	15.5
2-Hexanol	13.0	29.2
3-Hexanol	13.0	29.2
2-Methyl-1-pentanol	13.0	29.2
3-Methyl-1-pentanol	13.0	29.2
4-Methyl-1-pentanol	13.0	29.2

(continued)

APPENDIX 1 (continued).

Solute	$k \times 10^4$ cm/s	Sepn. %
3-Methyl-2-pentanol	13.0	53.1
2-Methyl-3-pentanol	13.0	53.1
3,3-Dimethyl-2-butanol	13.0	90.5
1-Heptanol	12.3	13.1
2-Heptanol	12.3	27.6
3-Heptanol	12.3	27.6
4-Heptanol	12.3	27.6
2-Methyl-3-hexanol	12.3	55.2
4-Methyl-3-hexanol	12.3	55.2
3-Methyl-3-hexanol	12.3	82.6
2,2-Dimethyl-1-pentanol	12.3	82.6
2,4-Dimethyl-3-pentanol	12.3	74.8
2,2-Dimethyl-3-pentanol	12.3	90.2
1-Octanol	11.7	11.2
2-Octanol	11.7	26.0
4-Octanol	11.7	26.0
5-Nonanol	11.2	24.8
Cyclohexanol	13.9	71.0
Aldehydes		
Acetaldehyde	19.5	44.5
Propionaldehyde	17.0	45.9
n-Butyraldehyde	15.3	47.7
i-Butyraldehyde	15.3	46.7
i-Valeraldehyde	14.0	47.8
Benzaldehyde	14.2	34.7
Hexanal	13.3	17.8
Ketones		
Acetone	17.0	27.8
Methyl ethyl ketone	15.3	29.5
2-Pentanone	14.0	34.1
Methyl isopropyl ketone	14.0	46.0
3-Pentanone	14.0	31.7
Cyclopentanone	14.3	53.3
Methyl n-butyl ketone	13.1	36.1
Methyl s-butyl ketone	13.1	44.3
Methyl i-butyl ketone	13.1	42.1
Methyl t-butyl ketone	13.1	58.9
Ethyl propyl ketone	13.1	36.6
Ethyl i-propyl ketone	13.1	40.1
Cyclohexanone	13.4	39.5
Methyl amyl ketone	12.4	21.5
Methyl i-amyl ketone	12.4	37.1
Dipropyl ketone	12.4	41.6
Diisopropyl ketone	12.4	49.3
Acetophenone	12.5	20.6
Dibutyl ketone	11.4	46.8
Diisobutyl ketone	11.4	59.2
Benzyl methyl ketone	11.9	24.7
Esters		
Methyl acetate	16.3	12.4
Ethyl acetate	14.8	16.0
Methyl propionate	14.8	14.3
n-Propyl acetate	13.7	20.4
2-Propyl acetate	13.7	27.7
Ethyl propionate	13.7	16.2
Methyl butyrate	13.7	20.5
Methyl 2-methyl-propionate	13.7	27.7
n-Butyl acetate	12.9	22.1
2-Methyl-1-propyl acetate	12.9	35.4
2-Propyl propionate	12.9	31.0
Ethyl butyrate	12.9	23.0
Ethyl 2-methyl-propionate	12.9	31.0
Methyl pentanoate	12.9	22.1
Methyl 2-methyl-butyrate	12.9	41.4
Methyl 3-methyl-butyrate	12.9	35.4
2-Methyl-1-butyl acetate	12.2	47.1
3-Methyl-1-butyl acetate	12.2	22.5
n-Butyl propionate	12.2	25.2
2-Propyl butyrate	12.2	41.2
2-Propyl 2-methyl-propionate	12.2	51.3
Ethyl pentanoate	12.2	25.2
Ethyl 2-methyl-butyrate	12.2	45.6
Ethyl 3-methyl-butyrate	12.2	39.5
Methyl caproate	12.2	12.3
Methyl 4-methyl-pentanoate	12.2	22.6
n-Hexyl acetate	11.6	6.4
n-Butyl butyrate	11.6	34.5
Ethyl caproate	11.6	14.2
Methyl heptanoate	11.6	6.4
2-Propyl caproate	11.2	27.9
Ethers		
Methyl propyl ether	14.9	42.9
Methyl isopropyl ether	14.9	56.3
Methyl butyl ether	13.8	46.0

(continued)

APPENDIX 1 (continued).

Solute	k×10^4 cm/s	Sepn. %
Ethyl propyl ether	13.8	47.7
Ethyl isopropyl ether	13.8	60.8
Methyl amyl ether	12.9	29.6
Ethyl butyl ether	12.9	51.3
Ethyl t-butyl ether	12.9	90.9
Dipropyl ether	12.9	62.3
Diisopropyl ether	12.9	82.4
Ethyl amyl ether	12.2	33.7
Isopropyl t-butyl ether	12.2	96.7
Anisole	13.6	21.5
Dibutyl ether	11.6	67.2
Diisobutyl ether	11.6	92.1
Phenetole	12.7	24.8
Carboxylic acids		
Acetic acid*	17.0	28.2
Propionic acid*	15.1	29.4
n-Butyric acid*	13.7	30.9
i-Butyric acid*	13.7	30.5
Valeric acid*	12.7	32.3
Pivalic acid*	12.7	65.2
Cyclohexane-carboxylic acid*	12.0	53.9
Benzoic acid*	12.8	22.2
Phenylacetic acid*	12.0	23.2
m-Toluic acid*	12.0	22.3
Anisic acid*	11.7	23.8
β-Phenylpropionic acid*	11.4	24.1
4-Phenylbutyric acid*	10.8	25.7
Oxalic acid*	15.8	95.6
Malonic acid*	14.4	66.3
Succinic acid*	14.0	56.9
Lactic acid*	14.4	79.0
D,L-Malic acid*	12.6	89.1
Tartaric acid*	12.3	97.0
Citric acid*	10.9	98.3
Polyfunctional compounds		
1,2-Ethanedoil	17.9	66.1
1,3-Propanediol	16.0	68.2
Propylene glycol	16.0	72.4
Glycerol	15.5	85.5
1,3-Butanediol	14.5	74.1
2,3-Butanediol	14.5	77.8
i-Erythritol	13.9	95.0
3-Hydroxy-2-butanone	15.0	58.2
1,5-Pentanediol	13.5	71.9
Arabitol	12.7	98.4
Xylitol	12.7	98.4
Adonitol	12.7	98.4
L-Arabinose	13.0	97.9
1,6-Hexanediol	12.7	55.5
cis- and trans-1,2-cyclohexanediol	13.5	89.2
trans-1,2-Cyclohexanediol	13.5	89.2
1,2,6-Hexanetriol	12.5	89.0
Pinacole	12.7	97.8
D-Sorbitol	11.9	99.5
Dulcitol	11.9	99.5
4-Hydroxy-4-methyl-2-pentanone	13.0	84.4
Acetonyl acetone	13.3	39.6
D-Glucose	12.1	99.3
D-Mannose	12.1	99.3
D-Galactose	12.1	99.3
D-Fructose	12.1	99.3
Sucrose	9.0	99.9
Maltose	9.0	99.9
Lactose	9.0	99.9

(continued)

*Separations data correspond to solute concentrations in feed = 200 ppm. See also NOTE at the end of Appendix.

APPENDIX 1 (continued).

(b) CALCULATED DATA ON REVERSE OSMOSIS SEPARATIONS OF DIFFERENT SOLUTES FOR THE PPPH-8273 MEMBRANE SPECIFIED IN TABLE 7

Operating conditions: very dilute feed solutions; Operating pressure: 405 psig; $k_{NaCl} = 20 \times 10^{-4}$ cm/s

Solute	$k \times 10^4$ cm/s	Sepn. %
NaCl	20	98.4
Inorganic Solutes		
CsBr	23.6	95.6
CsCl	23.5	95.6
CsI	23.5	95.6
LiBr	18.0	98.1
LiCl	17.9	98.1
LiF	16.5	98.5
LiI	18.0	98.1
KBr	23.3	95.8
KCl	23.0	95.7
KF	20.6	98.8
KI	23.1	95.8
RbBr	23.7	95.7
RbCl	23.5	95.7
RbI	23.5	95.8
NaBr	20.1	98.4
NaF	18.3	98.8
NaI	20.0	98.4
Alcohols		
Methanol	22.6	25.3
Ethanol	18.7	70.0
1-Propanol	16.5	80.2
2-Propanol	16.5	87.0
1-Butanol	15.0	83.9
2-Butanol	15.0	91.5
2-Methyl-1-propanol	15.0	86.9
2-Methyl-2-propanol	15.0	98.7
1-Pentanol	13.9	89.4
3-Methyl-1-butanol	13.9	94.6
3-Hexanol	13.0	94.7
2-Methyl-1-pentanol	13.0	94.8
3-Methyl-1-pentanol	13.0	94.5
4-Methyl-1-pentanol	13.0	95.9
3-Methyl-2-pentanol	13.0	97.1
2-Methyl-3-pentanol	13.0	98.4
3,3-Dimethyl-2-butanol	13.0	97.9
1-Heptanol	12.3	92.6
2-Heptanol	12.3	97.8
3-Heptanol	12.3	97.2
4-Heptanol	12.3	96.2
2-Methyl-3-hexanol	12.3	98.6
4-Methyl-3-hexanol	12.3	97.2
3-Methyl-3-hexanol	12.3	99.1
2,4-Dimethyl-3-pentanol	12.3	97.6
2,2-Dimethyl-3-pentanol	12.3	98.4
1-Octanol	11.7	90.8
Aldehydes		
Acetaldehyde	19.5	64.3
Propionaldehyde	17.0	72.2
n-Butyraldehyde	15.3	87.0
i-Butyraldehyde	15.3	93.2
i-Valeraldehyde	14.0	96.8
Benzaldehyde	14.2	75.0
Ketones		
Acetone	17.0	64.6
Methyl ethyl ketone	15.3	71.9
2-Pentanone	14.0	85.5
Methyl isopropyl ketone	14.0	93.0
3-Pentanone	14.0	78.4
Cyclopentanone	14.3	89.9
Methyl isobutyl ketone	13.1	94.2
Cyclohexanone	13.4	95.3
Diisopropyl ketone	12.4	98.4
Acetophenone	12.5	74.5
Diisobutyl ketone	11.4	99.6
Benzyl methyl ketone	11.9	87.8
Esters		
Methyl acetate	16.3	81.6
Ethyl acetate	14.8	86.3
Methyl propionate	14.8	86.4
n-Propyl acetate	13.7	93.3
2-Propyl acetate	13.7	96.1
Ethyl propionate	13.7	89.8
Methyl butyrate	13.7	93.3

(continued)

APPENDIX 1 (continued).

Solute	$k \times 10^4$ cm/s	Sepn. %
Methyl 2-methyl propionate	13.7	96.1
n-Butyl acetate	12.9	94.7
2-Methyl-1-propyl acetate	12.9	97.9
2-Propyl propionate	12.9	97.2
Ethyl butyrate	12.9	95.1
Ethyl 2-methyl-propionate	12.9	97.2
Methyl pentanoate	12.9	94.7
Methyl 2-methyl-butyrate	12.9	98.6
Methyl 3-methyl butyrate	12.9	97.9
2-Methyl-1-butyl acetate	12.2	99.1
3-Methyl-1-butyl acetate	12.2	94.8
n-Butyl propionate	12.2	96.3
2-Propyl butyrate	12.2	98.7
2-Propyl 2-methyl-propionate	12.2	99.3
Ethyl pentanoate	12.2	96.3
Ethyl 2-methyl-butyrate	12.2	99.0
Ethyl 3-methyl-butyrate	12.2	98.6
Methyl 4-methyl-pentanoate	12.2	93.5
n-Butyl butyrate	11.6	98.3
Ethers		
Ethyl butyl ether	12.9	93.5
Ethyl t-butyl ether	12.9	99.0
Dipropyl ether	12.9	96.1
Diisopropyl ether	12.9	98.7
Isopropyl t-butyl ether	12.2	99.7
Anisole	13.6	79.2
Phenetole	12.7	84.7

NOTE: Data on solute separations calculated above assume that, in each case, water is preferentially sorbed at the membrane-solution interface during reverse osomosis. Available knowledge on precise physicochemical criteria on preferential sorption at interfaces is still incomplete (3).

Nomenclature

A = pure water permeability constant, g-mol of $H_2O/cm^2 s$ atm
C, C_1^o, C_2, C_2^o, C_3, C_3^o and $\bar{C}_3$ = concentration ratios defined by eq. (32), (33), (34), (35), (36), (37), (38), and (39) respectively
C^*_{NaCl} = quantity defined by eq. (17)
c = molar density of solution, g-mol/cm^3
D_{AB} = diffusivity of solute in water, cm^2/s
$D_{AM}/K\delta$ = solute transport parameter (treated as a single quantity), cm/s
E_s, ΣE_s = Taft's steric constant for the substituent group in the organic molecule
$\Delta\Delta F^*$ = transition state free energy change
f = fraction solute separation defined by eq. (14)
$\bar{f}$ = average value of *f*
ΔG = free energy of hydration of solute, kcal/g-mol
ΔG_B, ΔG_I = value of ΔG for the bulk solution phase and membrane-solution interface respectively
$\Delta\Delta G$ = quantity defined by eq. (1)
$-\Delta\Delta G/RT$ = polar free energy parameter
h^{-1} = membrane area per unit volume of fluid space, cm^{-1}
k = mass transfer coefficient for the solute on the high pressure side of the membrane, cm/s
M_A, M_B = molecular weights of solute and water respectively
m = solute molality
N_A, N_B = solute flux and solvent flux respectively through membrane, g-mol/cm^{2}s
n_a, n_c = number of moles of anion and cation respectively in one mole of ionized solute
n_{hy} = number of moles of hydrolyzed species arising from the hydrolysis of one mole of solute
n_{ipa}, n_{ipc} = number of moles of anion and cation respectively in one mole of ion-pair
P = operating pressure, atm
PR = product rate through given area of membrane surface, g/h
PWP = pure water permeation rate through given area of membrane surface, g/h

R = gas constant

S = effective membrane area, cm^2

s^*, Σs^* = modified Small's number, $cal^{1/2}cc^{1/2}g\text{-}mol^{-1}$

Δs^* = quantity defined by eq. (5)

T = absolute temperature

t = time, s

$\overline{u}^o$ = average fluid velocity at membrane entrance, cm/s

V_1^o = initial volume of feed solution on the high pressure side of membrane, cm^3

v_s = permeation velocity of product solution, cm/s

v_w = permeation velocity of solvent water, cm/s

v_w^* = pure water permeation velocity, cm/s

X = quantity defined by eq. (40)

X_A = mole fraction of solute

x = longitudinal length of feed flow, cm

Z = quantity defined by eq. (49)

Greek Letters

α_D = degree of dissociation

α_H = degree of hydrolysis

α_n, α_p = nonpolar and polar parameters respectively characterizing polymer membrane materials

β = a parameter characterizing polymer membrane material, representing affinity of polymer material for nonionized polar organic solutes relative to that for an ionized inorganic solute

γ = quantity defined by eq. (28)

γ_B, γ_I = structural group contributions to ΔG_B and ΔG_I respectively

$\gamma_{B,0}$, $\gamma_{I,0}$ = constants in eq. (2) and (3) respectively

Δ = fraction product water recovery

$\ln\Delta^*$ = quantity defined by eq. (22) when polar, steric and nonpolar parameters are each set equal to zero

δ^* = coefficient associated with steric constant ΣE_s

θ = quantity defined by eq. (29)

$\pi(X_A)$ = osmotic pressure of solution corresponding to mole fraction X_A of solute, atm

τ = quantity defined by eq. (41)

ϕ = structural group contribution to $(\delta^*\Sigma E_s)_{lim}$

ϕ_o = constant in eq. (4)

ω^* = coefficient associated with modified Small's number Σs^*, $cal^{-1/2}\ cc^{-1/2}g\text{-}mol$

Subscripts

1 = bulk feed solution

2 = concentrated boundary solution on the high pressure side of membrane

3 = membrane permeated product solution on the low pressure side of membrane

Superscript

o = initial value, or value at membrane entrance

HYPERFILTRATION OF NONELECTROLYTES: DEPENDENCE OF REJECTION ON SOLUBILITY PARAMETERS

H. G. Spencer, J. L. Gaddis*

Abstract

The dependence of rejection of nonelectrolyte solutes in single-solute water solutions on solubility parameters is demonstrated using data from previously reported hyperfiltration studies. Solubility parameters characterizing the hyperfiltration systems are evaluated and a procedure for estimating the rejection of solutes from their solubility parameters is described.

SUMMARY

The dependence of hyperfiltration rejection of nonelectrolyte solutes in single-solute water solutions on solubility parameters is demonstrated using hyperfiltration results reported in the literature. The hyperfiltration systems are characterized by a solubility parameter derived empirically from the rejection-solubility parameter dependence. A criterion for high rejection follows.

INTRODUCTION

Hyperfiltration possesses high potential for separating toxic solutes in industrial unit operation effluents (ref. 1). Some of the nonelectrolytes of concern are quite volatile and many are only slightly soluble in water. Thus, the direct experimental measurement of the salt rejection R_i of the approximately 100 nonelectrolyte priority pollutants would be difficult and a reliable method for predicting R_i in a hyperfiltration system from a few reference measurements and molecular properties of the solutes i would be valuable.

The most detailed model developed for this purpose has been provided by Sourirajan and coworkers (ref. 2). Using one or more molecular properties (acidity, basicity, Hammett and Taft numbers, steric parameters, and Small's number) and the permeability and rejection of a reference solution, one can relate these properties to R_i. Other models use flux equations to relate the measurable properties of a hyperfiltration system (refs. 3,4). All approaches include both a transport property of the hyperfiltration system and a coefficient for the distribution of the solute between the bulk solution and the barrier.

We have previously pointed out the value of solute molecular weights in predicting R_i of nonelectrolytes (ref. 1). Most high rejection hyperfiltration membranes effectively reject nonelectrolytes with molecular weights greater than about 80. Cellulose acetate is an exception to this generalization. Although scatter can be large in plots of rejection vs. molecular weights, when the molecular weight is the most reliable or perhaps the only molecular property available it can be used to estimate R_i in systems characterized by a few measurements.

This report demonstrates a dependence of R_i for nonelectrolytes on the solute solubility parameter introduced by Hildebrand and Scott (ref. 5) and characterizes the hyperfiltration systems by solubility parameters. It also provides an empirical method for the rough estimation of R_i for a solute of known solubility parameter in a hyperfiltration system from values of R_i obtained for a few reference solutes without explicitly considering a transport property for the solute, providing its molecular volume is not vastly larger than those of the reference solutes.

Chian and Fang (ref. 6) proposed the difference between the solubility parameters of the solute and membrane plays the major role in determining R_i of nonelectrolyte solutes. Klein et al. (ref. 3) qualitatively related solute permeabilities in the absence of hydraulic flux with 2-dimensional solubility parameters and used the experimental permeabilities to predict specific separations of organic solutes under hyperfiltration conditions. A quantitative correlation of $\underset{\sim}{R}_i$ with solubility parameters was not attempted in either report.

---

*Departments of Chemistry and Mechanical Engineering, respectively, Clemson University, Clemson, SC.

DEFINITIONS, CONCEPTS, AND CALCULATIONS

The solubility parameter is defined by $\delta \equiv (\Delta\overline{E}/\overline{V})^{1/2}$ where $\Delta\overline{E}/\overline{V}$ is the energy of evaporation per unit volume, called the cohesive energy density. The units of δ are $(J/m^3)^{1/2}$. Solubility parameter theory predicts that the best solvent for a given solute, e.g., a polymer, is one whose solubility parameter is equal to or close to that of the solute (ref. 5).

The rejection $\underset{\sim}{R}_i$ of a solute is defined as $1 - C_p/C_b$, where C_p and C_b are concentrations in the permeate and bulk feed solutions respectively. An intrinsic rejection, $1 - C_p/C_w$, based on the concentrations of permeate and that occurring at the feed-membrane interface C_w is commonly defined. Normally the intrinsic rejection is projected as the infinite-velocity asymptote of the rejection $\underset{\sim}{R}_i$, and this intrinsic rejection is the property logically addressed in this study. Because most investigations are conducted so as to preclude large differences in the two rejections, and virtually no data exist projecting the intrinsic rejection, the observed rejection is used throughout. Errors produced by this simplification may be substantial and are largest near rejections of 0.5.

In hyperfiltration the distribution of solute between the bulk solution and the barrier is assumed to be important in determining $\underset{\sim}{R}_i$. Further, assuming the concentration of solute available for transport across the hyperfilter depends on $\Delta_{im} = \delta_i - \delta_m$, where δ_m characterizes the hyperfilter, $\underset{\sim}{R}_i$ should be a function of Δ_{im}. Of course, an attempt to relate $\underset{\sim}{R}_i$ to Δ_{im} alone is incomplete because a transport property characterizing the hyperfiltration system is not explicitly included.

The group contribution method of Konstam and Fairheller (ref. 5) was used to calculate Small's number (ref. 8) S_i and the δ_i were obtained by $\delta_i = S_i/\overline{v}_i$ where $\overline{v}_i$ is the molar volume. This method is used although tables containing δ_i for many solutes are available (refs. 5,9). It is desirable to use a consistent method for as many compounds as possible. Even with the use of this general approach some values of δ_i are not available, especially those for polyfunctional molecules. Values of $\overline{v}_i$

TABLE 1. CHARACTERISTICS OF HYPERFILTRATION SYSTEMS

Membrane	Pressure (MPa)	Temperature (° C)	$10^{-3}\ \delta_m$ $(J/m^3)^{1/2}$	Classes of solutes	Reference
Aromatic polyamide	1.72	25	29.0	Alcohols, aldehydes, ethers, ketones	11
Aromatic polyamide, Permasep B-9, hollow fiber	3.10	20	30.0	Alcohols, acids	12
Cellulose acetate	1.72	25	25.0	Alcohols, aldehydes	11
Cellulose acetate	1.72	23-25	25.0	Alcohols, aldehydes, esters, ethers, hydrocarbons	15
NS-100	5.52	25	34.5	Acids, alcohols, aldehydes, esters, ketones, amines	13
Poly(ether/amide) PA-300	6.89	25	(~34)†	Acid, alcohols, aldehydes, esters, ketone, chlorohydrocarbons	14

†Not enough data for extrapolation.

were calculated by dividing molecular weight of the solute M_i by its density ϱ_i in the liquid state at the temperature of the experiment, with M_i and ϱ_i obtained from commonly used tables (ref. 10).

DEPENDENCE OF REJECTION ON SOLUBILITY PARAMETERS

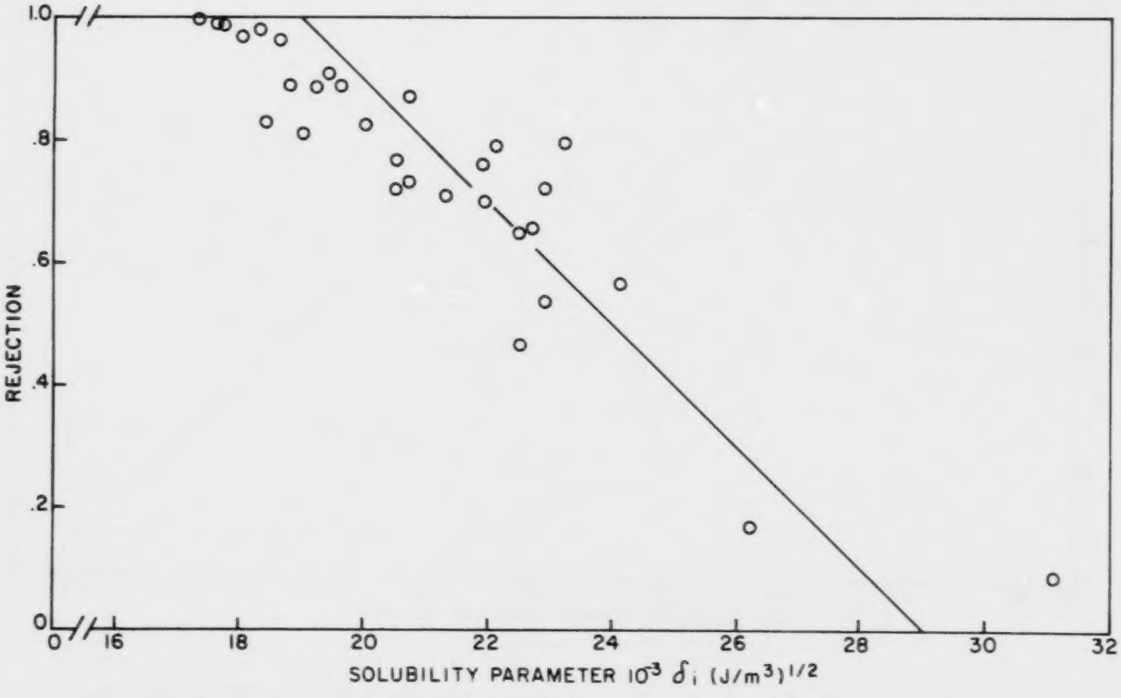
Figures 1 through 5 show the dependence of R_i on δ_i for the six hyperfiltration systems described in Table 1 (refs. 11,12,13,14,15). The δ_i occurring at $R_i = 0$ is assumed to be the solubility parameter characterizing the membrane system and is designated δ_m. The δ_m values were obtained by a visual linear extrapolation of the plots. A slope of -10×10^{-3} $(m^3/J)^{1/2}$ was satisfactory for all graphs in the region $\Delta_{im} < 0$. Insufficient data are provided to determine δ_m by extrapolation in the poly(ether/amide) thin film composite (PA-300) system, Figure 4. Using the slope observed in the remainder of the graphs, δ_m should be in the interval $34 \times 10^3 < \delta_m < 36 \times 10^3 (J/m^3)^{1/2}$. It should be noted that the scatter is very large in the cellulose acetate systems.

In the Permasep B-9 and cellulose acetate systems (see Figures 2 and 5), several values of R_i at $\Delta_{im} > 0$ are available. It is clear in Figure 2 that R_i increases monotonically with increasing Δ_{im} in the region $\Delta_{im} > 0$. The dependence is not well defined in the cellulose acetate case where in this region several of the solutes listed contain two functional groups and the calculation of δ_i is less reliable.

The molecular weight, or $\overline{v}_i$, may be used to estimate R_i in many systems, however this dependence appears to be absent in the cellulose acetate system. Figure 6 is provided to illustrate this observation and it should be compared with Figure 5, where the R_i values are plotted vs. δ_i.

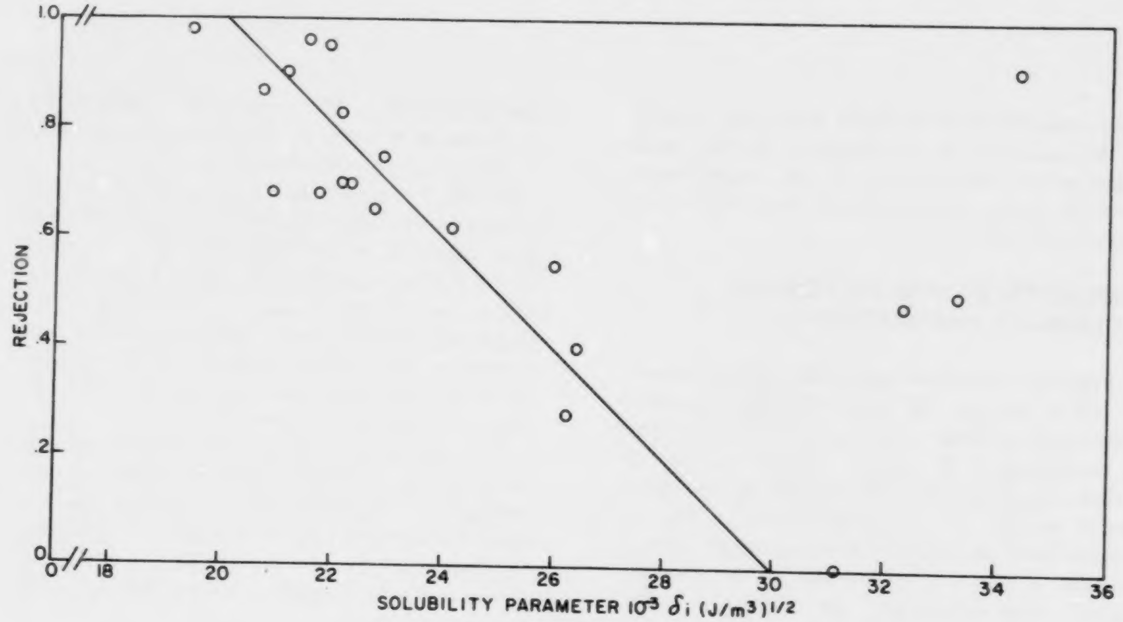
DISCUSSION

The dependence of R_i on δ_i has been il-



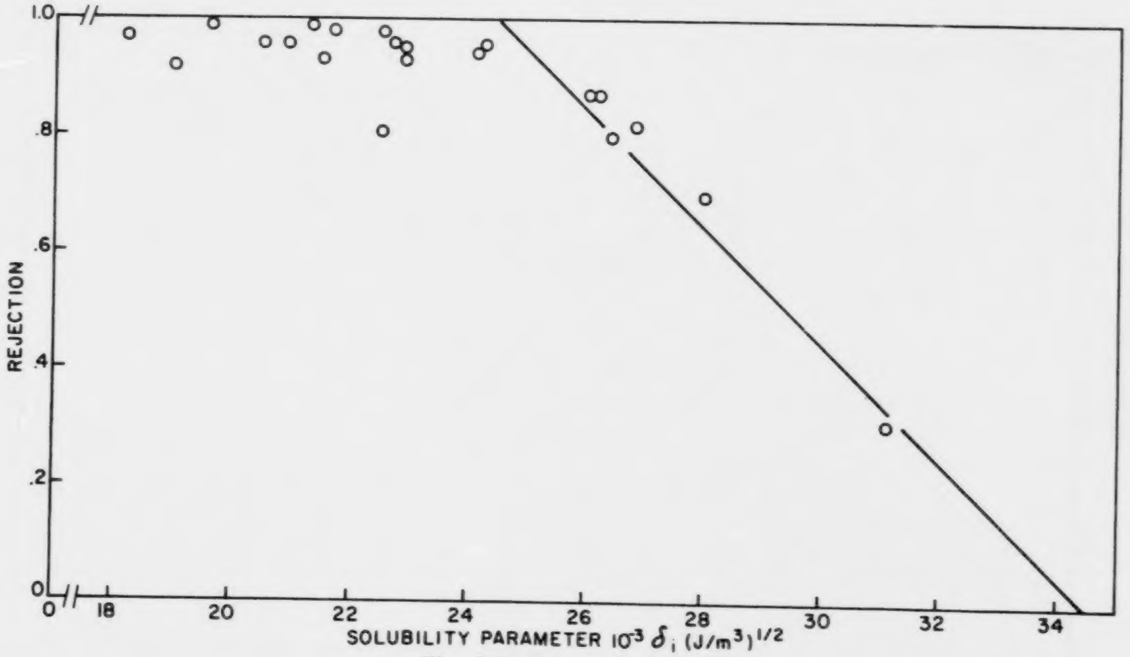
Polyamide Membrane, 1.72 MPa, 25°C

Figure 1. Solute rejection vs. solubility parameter: Polyamide membrane, 1.72 MPa, 25° C (ref. 11).



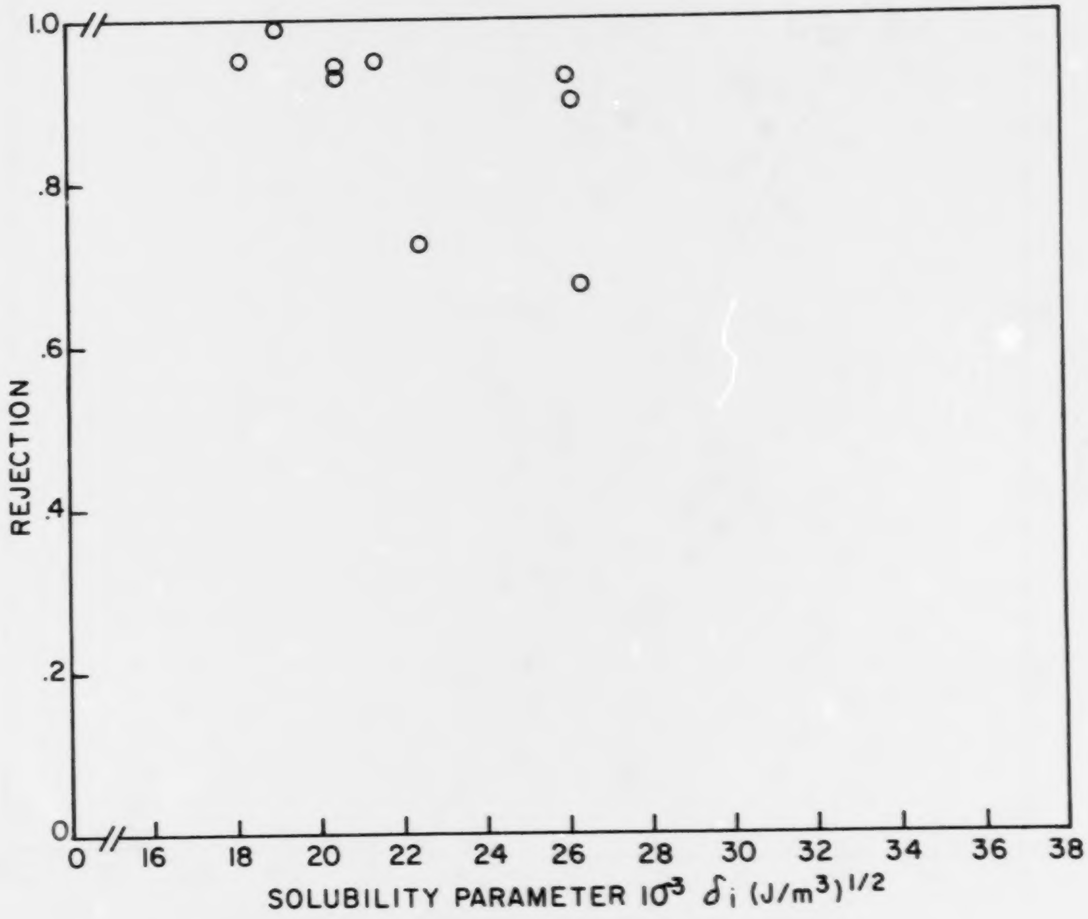
Polyamide, Permasep B-9, 3.10 MPa, 20°C

Figure 2. Solute rejection vs. solubility parameter: Polyamide, Permasep B-9, 3.10 MPa, 20° C (ref. 12).



NS - 100, 5.52 MPa, 25°C

Figure 3. Solute rejection vs. solubility parameter: NS-100, 5.52 MPa, 25° C (ref. 13).



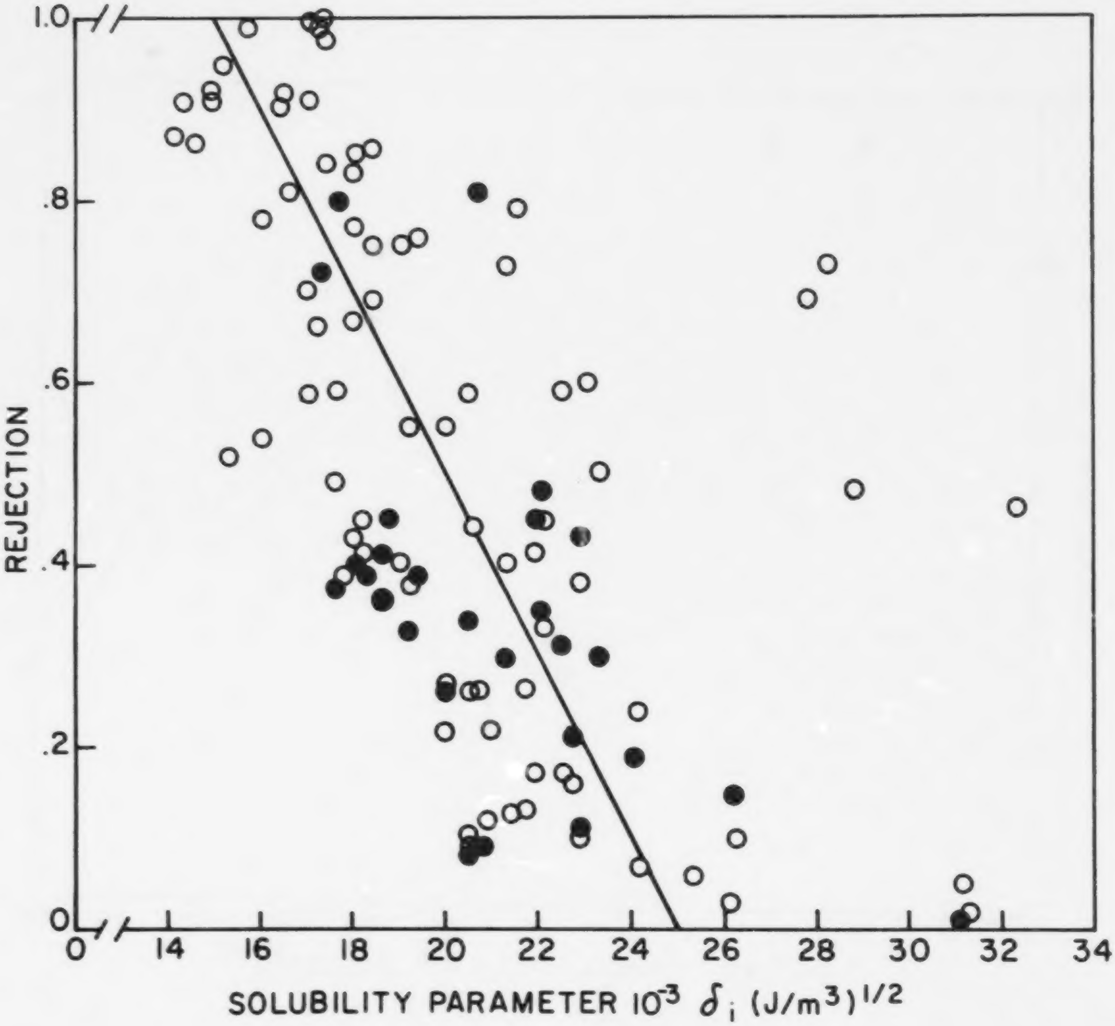
PA - 300, 6.89 MPa, 25°C

Figure 4. Solute rejection vs. solubility parameter: poly(ether/amide), PA-300, 6.89 MPa, 25° C (ref. 14).

lustrated in several hyperfiltration systems. It is evident that high rejection occurs when Δ_{im} is large. Figure 7 provides a graph of R_i vs. Δ_{im} for all the membranes other than the cellulose acetate membranes and Figure 5 provides a graph of R_i vs. δ_i for the cellulose acetate systems, where the scatter is greater.

This empirical treatment of rejection of nonelectrolytes in hyperfiltration systems also provides a method for estimating R_i for any solute of known δ_i from a few reference experiments. The value of δ_m is determined from a graph of R_i vs. δ_i obtained for the reference solutes. Solutes having $\Delta_{im} < -10 \times 10^3$ $(J/m^3)^{1/2}$ should have $R_i > 0.90$. In the region $-10 \times 10^3 < \Delta_{im} < 0 (J/m^3)^{1/2}$, $R_i \approx -10 \times 10^{-3}\ \Delta_{im}$, this estimate being better for membranes other than cellulose acetate.

The value of δ_m appears to characterize the hyperfiltration system with respect to its rejection of nonelectrolytes and provides an attractive criterion for selecting membranes for hyperfiltration applications. Although the nonelectrolyte priority pollutants possess a broad range of solubility parameters, the maximum appears to be about 28 × $10^3 (J/m^3)^{1/2}$ and many



Cellulose Acetate, 1.72 MPa, 23-25°C

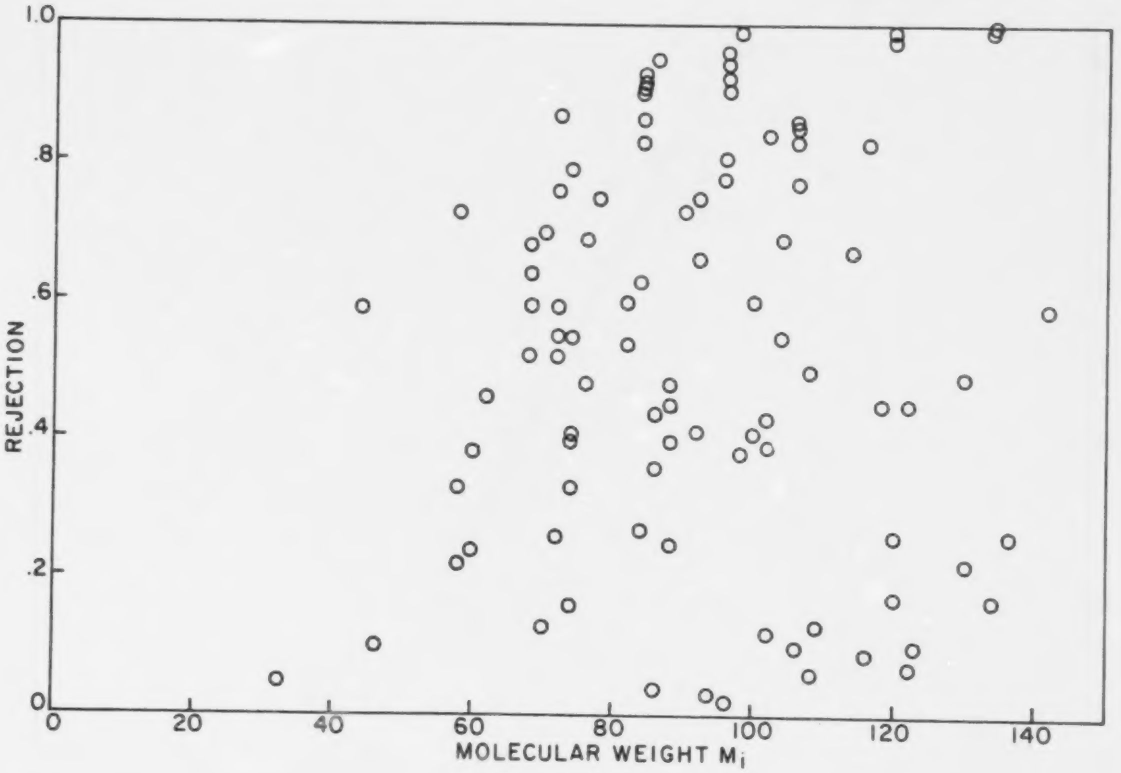
Figure 5. Solute rejection vs. solubility parameter: cellulose acetate, 1.72 MPa, 23-25° C (refs. 11, 15).

are much smaller. Hyperfiltration systems with δ_m greater than 36×10^3 or 38×10^3 $(J/m^3)^{1/2}$ should provide high rejections of these solutes.

Refinement of this approach using solubility parameters as a measure of the membrane-solute interaction will likely require incorporation in a flux model.

ACKNOWLEDGMENT

The authors wish to acknowledge the generous financial support of this work by the U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, NC, EPA Grant Number R805777-1.

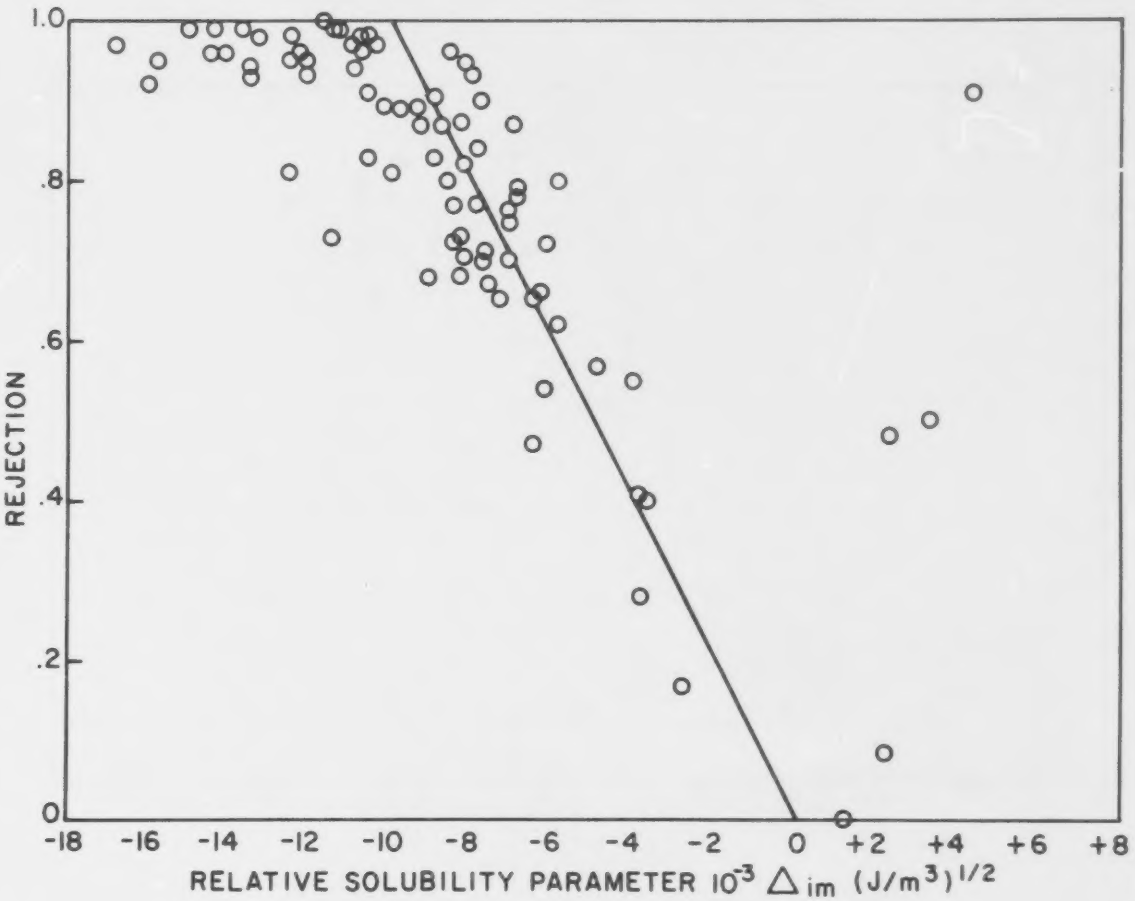


Cellulose Acetate, 1.72 MPa, 23-25°C

Figure 6. Solute rejection vs. molecular weight: cellulose acetate, 1.72 MPa, 23-25° C (ref. 15).

REFERENCES

1. H. G. Spencer, J. L. Gaddis, and C. A. Brandon, "Membranes for Toxic Control," presented at the Membrane Separation Technology Seminar, Clemson University, Clemson, SC, 1977.
2. S. Sourirajan and T. Matsuura, "Reverse Osmosis and Synthetic Membranes," S. Sourirajan, ed., National Research Council of Canada Publications, Ottawa, Canada, Chapter 2, 1977.
3. K. S. Spiegler and O. Kedem, *Desalination*, Vol. 1, p. 311, 1966; H. K. Lonsdale, U. Merten, and R. L. Riley, *J. Appl. Polymer Sci.*, Vol. 9, p. 1341, 1965; and L. Dresner and J. S. Johnson, Jr., *Principles of Desalination*, 2nd ed., K. S. Spiegler and A. D. K. Laird, eds., Academic Press, New York, in press.
4. E. Klein, J. Eichelberger, C. Eyer, and J. Smith, *Water Res.*, Vol. 9, p. 807, 1975.
5. J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Rheinhold, New York, 1950.
6. E. S. K. Chian and H. H. P. Fang, AIChE Symposium Ser., Vol. 70, p. 497, 1973.
7. H. H. Konstam and W. R. Fairheller, Jr., *AIChE J.*, Vol. 16, p. 837, 1970.
8. P. A. Small, *J. Appl. Chem.*, Vol. 3, p. 71, 1953.
9. J. L. Gordon, *Encyclopedia of Polymer Science and Technology*, Vol. 3, p. 833, 1965; H. Burrell, *J. Paint Technol.*, Vol. 27, p. 726, 1955; C. M. Hansen, *Ind. Eng. Chem., Prod. Res. Dev.*, Vol. 8, No. 2, 1960.



Noncellulosic Membranes

Figure 7. Solute rejection vs. relative solubility parameter $\Delta im = \delta i - \delta m$ for the noncellulosic membranes.

10. *Handbook of Chemistry and Physics*, R. E. Weast, ed., CRC Press, Inc., Cleveland, OH.
11. J. M. Dickson, T. Matsuura, P. Blais, and S. Sourirajan, *J. Appl. Polymer Sci.*, Vol. 19, p. 801, 1975.
12. V. B. Caracciolo, N. W. Rosenblatt, and V. J. Tomsic, "Reverse Osmosis and Synthetic Membranes," S. Sourirajan, ed., National Research Council of Canada, Ottawa, Canada, Chapter 16, 1977.
13. L. T. Rozelle, J. E. Cadotte, K. E. Cobian, and C. V. Kopp, Jr., "Reverse Osmosis and Synthetic Membranes," S. Sourirajan, ed., National Research Council of Canada, Ottawa, Canada, Chapter 12, 1977.
14. R. L. Riley, R. L. Fox, C. R. Lyons, C. E. Milstead, M. W. Seroy, and M. Togami, "Spiral-wound Poly (ether/amide) Thin-film Composite Membrane Systems," presented at the Membrane Separation Technology Seminar, Clemson University, Clemson, SC, 1976.
15. T. Matsuura and S. Sourirajan, *J. Appl. Polymer Sci.*, Vol. 15, p. 2905, 1971; *J. Appl. Polymer Sci.*, Vol. 16, pp. 1663 and 2531, 1972; *J. Appl. Polymer Sci.*, Vol. 16, pp. 1043 and 3683, 1973.

SEPARATION OF TOXIC SUBSTANCES BY HYPERFILTRATION*

J. Leo Gaddis, H. Garth Spencer[†]

Abstract

Experiments have been run to determine the separation of toxic substances in textile water streams when subjected to hyperfiltration. The data indicate a high level of separation of toxic substances by hyperfiltration. Three membranes of commercial significance were tested: cellulose acetate, poly (ether/amide) thin film composite, and the dynamic membrane. The membranes were exposed to textile streams from mild caustic scouring and from dyeing of cotton. Data regarding the separation of priority pollutants are presented according to chemical analysis of samples. Also presented are data from biological testing with fathead minnows and daphnia. Acute rat toxicity, hamster ovary clonal assay, and Ames tests are included. Separation in LC_{50} *from a level of 55 to 100 percent is produced in actual textile test fluids.*

INTRODUCTION

Hyperfiltration membranes may have the capability of separating toxic substances in textile process water. The literature contains measurements of membrane rejections of ionic and nonionic materials, but there are only a few data on the rejection of toxic pollutants except for metals. This program was initiated to determine the separation characteristics of membranes for process stream toxicity (determined from bioassay) and for toxic pollutants (determined by analysis).

Toxic materials that enter a process stream may have various origins. Field-applied agricultural chemicals on cotton, spinning oils on synthetics, warp size chemicals on cotton woven goods, and preparation and dyeing solutions are examples. The fluids selected for study were from preparation and dyeing of cotton goods. Three membranes were selected: cellulose acetate (CA), poly ether/amide (PEA), and a dynamic zirconium oxide/poly acrylic acid membrane (DM). The basis for selection was reasonable expectation of applicability to industrial streams and commercial availability.

TEST DESCRIPTION

Figure 1 shows a schematic of the fluid collection and test apparatus. Fluid from the second washer of the range was pumped to the test apparatus. Prior experience indicated the fluid to be representative of the average fluid from the range, not the highest nor lowest concentration of the individual streams emanating from the range. The fluid was prefiltered using a 1-μ polypropylene cartridge filter for removal of suspended materials, except for the dynamic membrane runs where prefiltration is not required.

An initial feed volume of about 600 liters was pressurized in a plunger pump to feed the membranes. The membrane feed was concentrated slightly by the membrane as it passed through the assembly. The concentrated feed was returned to the feed reservoir, and the permeate(s) collected in separate containers. The original feed was thus gradually diminished in volume until 10 to 20 percent of its original volume was remaining. This residual comprised the concentrate fluid. A straightforward excercise indicates that this procedure produces permeate and concentrate samples equivalent to those expected in a prototype unit.

Four tests were run: (1) PEA and CA simultaneously operating on dye fluid, (2) DM operating on dye fluid, (3) PEA and CA simultaneously operating on scour fluid, and (4) DM operating on scour fluid. Feed, permeate, and concentrate samples were taken on each run. In addition, samples were taken for chemical analysis of the plant supply water and for water passed through the range and circulated in the apparatus.

The scour-fluid known chemicals are the

---

*Work sponsored by EPA Grant 805777, Dr. Max Samfield, Project Officer.

[†] Departments of Mechanical Engineering and Chemistry, respectively, Clemson University, Clemson, SC.

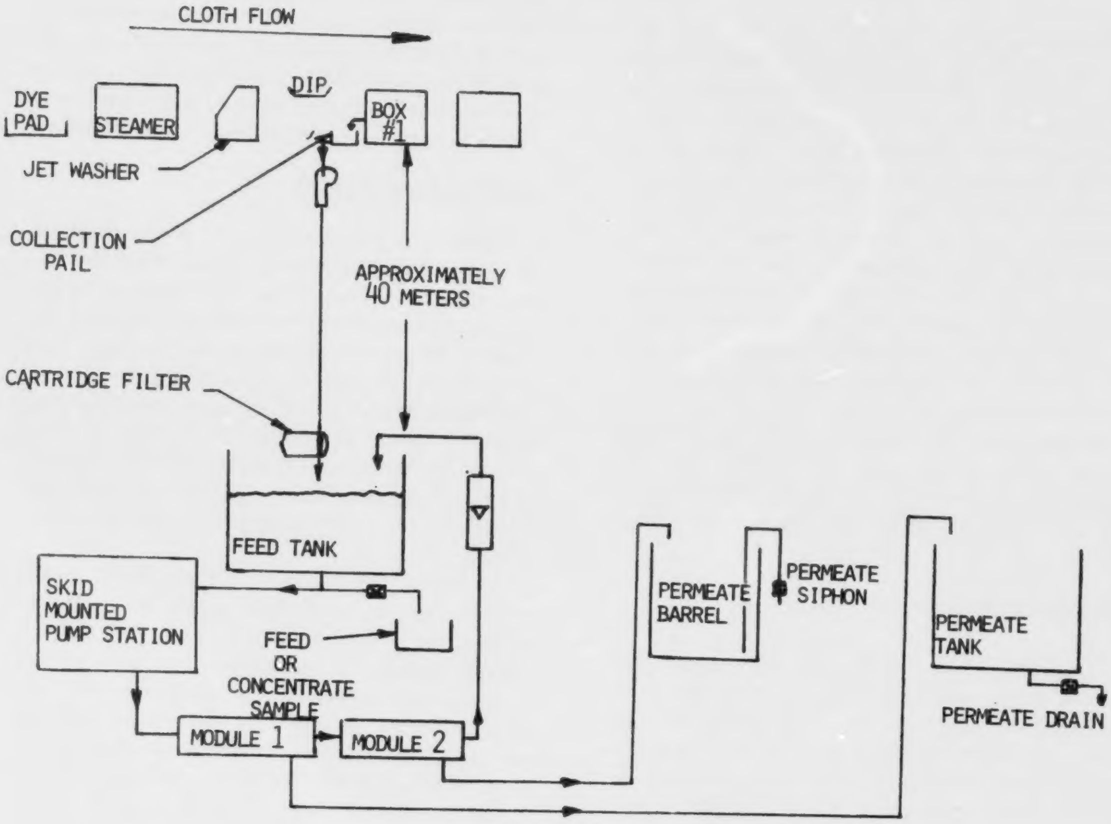

CLOTH FLOW
DYE PAD
STEAMER
DIP
BOX #1
JET WASHER
COLLECTION PAIL
APPROXIMATELY 40 METERS
CARTRIDGE FILTER
FEED TANK
SKID MOUNTED PUMP STATION
FEED OR CONCENTRATE SAMPLE
MODULE 1
MODULE 2
PERMEATE BARREL
PERMEATE SIPHON
PERMEATE TANK
PERMEATE DRAIN

Figure 1. Schematic of fluid acquisition and operations.

warp size removed in the scour, a detergent/wetting agent, hydrogen peroxide, and sodium carbonate. Residuals of field chemicals, motes on the cotton fiber, and natural oils and waxes may also be present. The dye fluids contain a thickener (gum), two detergent/wetting agents, and a particular mixture of direct dyes.

RESULTS

In general, all membranes performed according to expectations. Rejection (fraction removed) of color was nearly perfect (>99 percent); rejection of total solids averaged 94 percent (88 to 98 percent); and rejection of conductivity averaged 95 percent (85 to 99 percent). Analyses for specific toxic organic and metal compounds were performed by Monsanto Research Corporation under a separate grant with EPA. The detailed results are contained in the project final report (ref. 1) and are summarized here. Only 19 organic compounds were sensed; the highest concentration was below 300 mg/m^3. Analysis in this low concentration range is not expected to be more than modestly accurate, effectively precluding a meaningful calculation of rejection. However, it appears that chloroform, toluene, trichloroethylene, and methylene chloride were not effectively rejected. Phenol and di-n-Butyl phthalate showed a mixed tendency to be rejected. The other compounds were shown to be rejected and are: bis(2-ethylhexl) phthalate, dimethyl phthalate, butylbenzyl phthalate, diethyl phthalate, acenaphthene, anthracene, fluoranthene, pyrene, naphthalene, phenanthrene, chlorobenzene, and ethylbenzene. The basis for rejection, or no rejection, for all the above is relatively weak. Some of the compounds may have vaporized, others may have been coated on the apparatus surfaces, and still others may have been rendered nonextractable for analysis. Mass balances of solutes were mostly poor.

Toxic metals were also present only in low concentration. Adequate concentrations for analysis of only arsenic, copper, and zinc occurred. All these metals were rejected well. Arsenic (one point has rej>69) rejection averaged 89 percent, copper averaged 97 percent, and zinc 100 percent. Other nontoxic metals were analyzed and showed high rejection.

Rat acute toxicity and microbial mutagen-

TABLE 1. LETHAL CONCENTRATION AND IMPLIED TOXICANT CONCENTRATIONS

	96-h minnows			48-h daphnia	
Fluid and type	Sample no.	LC$_{50}$ % solution	Implied concentration no. units	LC$_{50}$ % solution	Implied concentration no. units
Dye-feed	10	9.7	10	33.5	3.0
Dye-pea permeate	11	82	1.2	60 to 100	1 to 1.7
Dye-CA permeate	12	>100	<1	60 to 100	1 to 1.7
Dye-concentrate	13	1.6	62	4.1	24
Dye-feed	14	25	4	49	2.0
Dye-DM permeate	15	NAT	0	80	1.2
Dye-concentrate	16	5.3	19	17	5.9
Scour-feed	3	16	6	26	3.8
Scour-pea permeate	4	28	3.6	53	1.9
Scour-CA permeate	5	>100	<1	42	2.4
Scour-concentrate	6	1.5	67	5.1	20
Scour-feed	7	13	7.7	25	4
Scour-DM permeate	8	NAT	0.0	>100	1
Scour-concentrate	9	2.0	50	9.9	<10

TABLE 2. REJECTION OF TOXICITY BY HYPERFILTRATION

Membrane	% Rejection	
	Daphnia toxicant	Fathead minnow toxicant
Scour fluid		
Dynamic ZrO/PAA	>88	100
Cellulose acetate	55	>92
Poly ether/amide	68	60
Dye fluid		
Dynamic ZrO/PAA	60	100
Cellulose actate	62 to 82	>96
Poly ether/amide	62 to 82	95

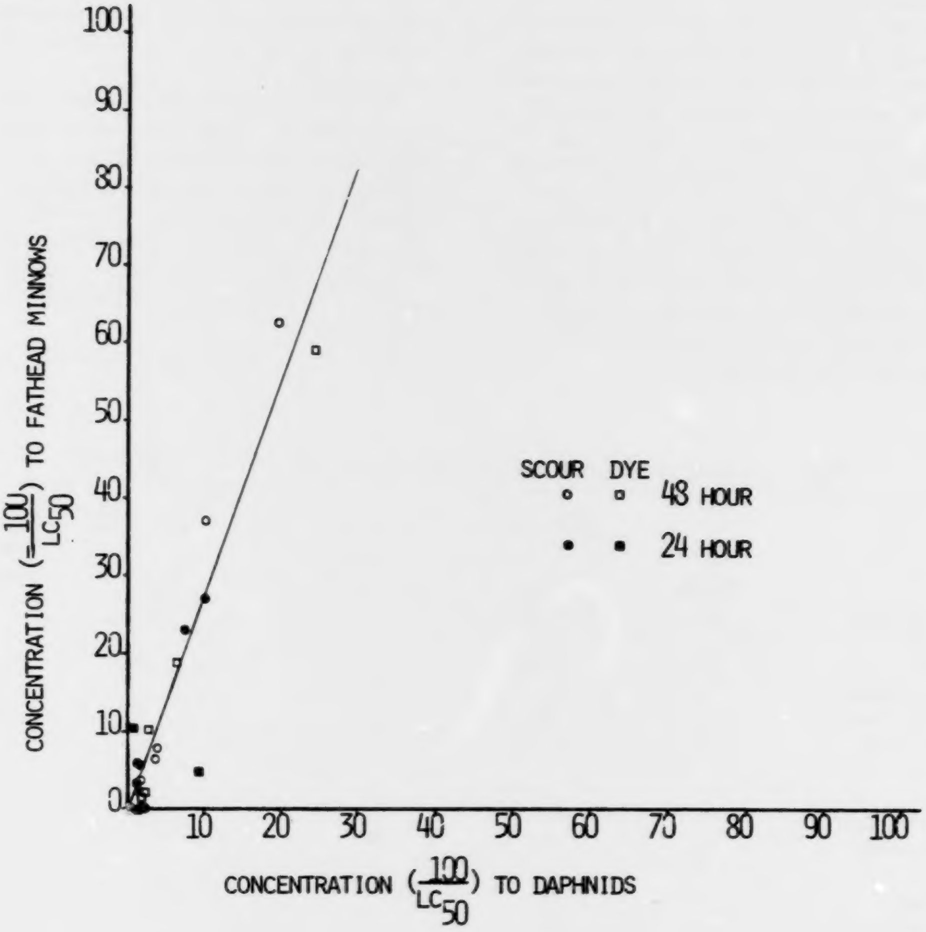


Figure 2. Correlation of concentration toxic to fathead minnows with concentration toxic to daphnids.

icity bioassays showed no effect. Hamster ovary clone cytotoxicity showed effects on the concentrate samples only. Results of acute studies with daphniids and fathead minnows showed consistent, interesting results. Table 1 shows the results obtained for LC_{50}(concentration of sample in water was lethal to half the test subjects) at 96 hours for minnows and 48 hours for daphniids. Also shown in the table is the corresponding value of $100/LC_{50}$, which is the number proportional to the concentration for the toxicant in the sample. Use of this implied concentration allows calculation of mass balance of toxicant and rejection of toxicant by regular procedures. It is acknowledged that such a calculation may oversimplify the problem.

Using the implied concentrations for the four test runs allows mass balances of toxicant to be calculated as 0.95, 1.28, 1.55, and 1.17 (minnow data), and 1.16, 1.23, 1.08, 0.65 (daphniid data). These values are highly consistent compared to expectations and are almost as good as those obtained for total solids. Table 2 shows the rejection data corresponding to the bioassay. The average rejection of daphniid toxicant is 69 percent, and minnow toxicants is 90 percent. The relative membrane effectiveness for removal of toxicant is DM > CA > PEA, while for salt removal the relative order is PEA > CA > DM.

There is a high correlation of the data obtained for daphniid and minnow toxicity. Figure 2 shows the results of both 24- and 48-h responses as reciprocal LC_{50} for each animal. The correlation coefficient for the data is 0.94, suggesting an excellent empirical relationship.

CONCLUDING REMARKS

Hyperfiltration has been shown to be an effective separator for toxic materials in textile process streams. The bioassay data for daphniids and minnows provide consistent evidence of high separation of about 70 percent for daphniids and 90 percent for minnows.

Because of analytical difficulties associated with low concentrations, most of the organic and metal toxic pollutant rejections were not determined. There is good evidence, in agreement with prior experience, for high rejection of metals. Some organics were rejected badly or not at all, but most were separated. Further studies under controlled conditions should be undertaken to determine the separation of these materials.

REFERENCES

1. J. L. Gaddis and H. G. Spencer, *Evaluation of Hyperfiltration for Separation of Toxic Substances in Textile Water Process Water,* final report, Grant R805777, to be printed by EPA.

Session III: AIR POLLUTION CONTROL TECHNOLOGY

Donald F. Walters, Session Chairman

Preceding page blank

INCINERATION AND HEAT RECOVERY IN THE TEXTILE INDUSTRY

William H. Hebrank*

Abstract

The paper discusses ways to solve air pollution and excess fuel uses caused by textile dryer exhausts. Heat recovery with incineration minimizes heat exchanger cleaning maintenance and provides net fuel savings, even without exhaust reduction. Five purposes for exhaust size are presented, along with parameters to evaluate the size of a dryer's exhaust. The three mechanisms of incineration described are flame exposure, thermal, and catalytic. In increasing order of complexity, five different types of incinerators in industrial use are described. These are the dryer counterflow incinerator, the afterburner incinerator, the incinerator with a preheater, the recycling loop incinerator, and the high-temperature thermal incinerator.

The subject of this paper is incineration with heat recovery applied to exhaust gases from textile finishing dryers. Textile finishing dryer exhausts are a problem for two reasons. First the exhaust is a relatively large flow, usually about 9,000 to 18,000 kg of air per hour, and it is hot enough to cause a large heat loss. The reduction of large heat losses from dryer exhausts is the most important fuel conservation task in the textile industry. The second problem with textile dryer exhaust relates to air pollution. The blue haze and odor from many finishing dryer exhausts takes first place as the most important air pollution problem in the textile industry.

The amount of air pollution from dryer exhaust stacks depends on the finishing process. Various kinds and amounts of oils and finishing resins are vaporized from the cloth in dryers at high drying and cloth setting temperatures. Some exhausts also carry quite a bit of lint. There are process means to reduce some of the air pollution. Nowadays, most of the oils are removed by a prescour process and, sometimes, the use of a vacuum slice before the dryer decreases the amount of resin on cloth entering the dryer. Alternate selection of finishing chemicals may also help, but cloth finish quality and economics limit the ability of processes to correct the problem.

Most dryers use natural gas for fuel. If the dryer exhaust is clean exhaust, heat recovery should be used to save fuel. A good exhaust heat recovery application can pay for itself in 1 to 2 years. With gas prices going up, it is economically foolish to put off heat recovery plans. However, in most cases, unless heat recovery equipment can be easily cleaned, condensing smoke from the exhaust stream soon plugs heat transfer surfaces and diminishes economic gains.

If the exhaust can be cleaned of dirt and smoke from lint and condensing oils before passing heat-recovery heat exchangers, the prospects for success are greatly improved. Unfortunately, air-cleaning devices such as scrubbers or electrostatic precipitators require cooling the exhaust before cleaning so we are back to problems with heat exchanger plugging. Incinerators have an advantage. The sequence is reversed; exhaust is cleaned before going to heat recovery. That point, plus the fact that burning is the most convenient way to get rid of air polluting smoke, makes incineration very attractive.

You may have heard that incineration requires additional fuel use. That just is not so; a properly designed incineration system with heat recovery can reduce the total fuel used for drying. Depending on circumstances, the savings can run as high as 60 to 65 percent. It is possible to get 15 to 25 percent savings, even without any exhaust reduction.

It is important to review the size of the existing exhaust flow rate before planning to install exhaust air pollution and heat recovery equipment. Size and cost of equipment depends on the amount of exhaust flow. Many exhausts can be reduced, sometimes by as much as 50 percent. Exhaust reduction also concentrates

---

*Hebrank Incorporated, Greenville, SC.

Preceding page blank

smoke and vapors in the exhaust steam, thus making them easier to remove. The amount of exhaust needed depends on the cloth drying-finishing-setting process, the rate of cloth flow, the dryer's tightness against smoke leakage, and plant operating-room ventilation conditions.

In considering the amount of a textile dryer exhaust, remember that there are at least five purposes for that exhaust, the first of which is to decrease evaporated water vapor concentration in the dryer housing. Exhaust should be thought of in terms of decreasing concentration; not in terms of removing water vapor. It can not remove all of the evaporated water; it serves to bring water vapor concentration down to levels consistent with good operation. Many dryers use more than 30 kg of exhaust to carry off 1 kg of evaporated water. This can be reduced to the 16- to 18-kg range. I have heard it said that with extensive effort to seal the dryer and control plant conditions on some dryers, one can reach 10 to 12 kg without noticeably affecting drying rates. The paper industry has known this with their high speed dryers for years.

The second purpose for exhaust is to decrease the concentration of process smoke and vapors in the dryer. Again all smoke cannot be removed. Fresh makeup air to replace air leaving as exhaust dilutes the concentration. As concentration goes down, additional exhaust has less and less benefit.

The third purpose of exhaust is to reduce dryer pressure below room air pressure to maintain a slight inflow to all dryer openings from the room. Water vapor and smoke gases generated from the cloth add their partial pressures to the total inside the dryer and must be accounted for in exhaust calculations. Local high pressure areas due to circulation flows inside the dryer make it more difficult to maintain a slight inflow at all dryer openings. The inflow of air aspirates and cleans air near the openings, not unlike a ventilation hood over a shop welding or grinding operation. Also, the partial pressure of fumes inside the dryer is higher than the partial pressure of fumes in the room. This difference of partial pressure causes fumes to diffuse or flow towards the room's lower concentration level. With a very slow inflow air stream, the fume diffusion rate may be fast enough to swim against the inflowing air and, thus, cause smoke or haze to occur in the room.

The fourth purpose for exhaust is to remove products of combustion from the dryer burners. The fifth purpose is to properly ventilate the dryer during startup prior to the ignition.

Textile dryer exhaust dirt and smoke are organic compounds. They can be destroyed by burning, that is reduced to mostly carbon dioxide and water vapor, with three different incineration mechanisms. The first mechanism is by direct exposure to flames. For efficient operation, design of conditions around the combustor such as control of flame geometry and airflows are most important. The flame front itself is a highly ionized and reactive region and should be used to best advantage. Temperature level is not that important but should be at least 320° to 340°C.

The second incineration mechanism is the phenomena of thermal ignition. Flames are not necessary for a substance to thermally ignite. If a combustible substance in air is hot enough it will go through the chemical reactions to oxidize to mostly carbon dioxide and water vapor. Thermal ignition temperatures of various organic compounds in air are listed in chemical handbooks. Most of the common solvents have thermal ignition temperatures in the 320° to 590°C range. If essentially all of the substances in exhaust smoke thermally ignite at 510°C or lower, it makes little sense to go to 650° or 820°C in the incinerator. A rule of thumb for thermal incinerators is to heat exhaust to 650° to 820°C and maintain the temperature for one-half second or so. Those high temperatures require expensive high-temperature materials, and the incinerator uses more fuel at high temperatures. In taking the overall environment and available resources into consideration, the aim should be to do an adequate job of cleaning exhaust. It can be wrong and wasteful to aim for a 100 percent cleaning operation.

The third mechanism for incineration is to accomplish chemical reactions of the dryer smoke substances at the surface of a catalytic material. Chemical reaction rates are related to temperature and surface conditions. At the catalytic interface, reaction rates go faster, thus allowing a reduction of temperature with attendant savings on materials and fuel usage. Catalytic reactors are costly and, with certain

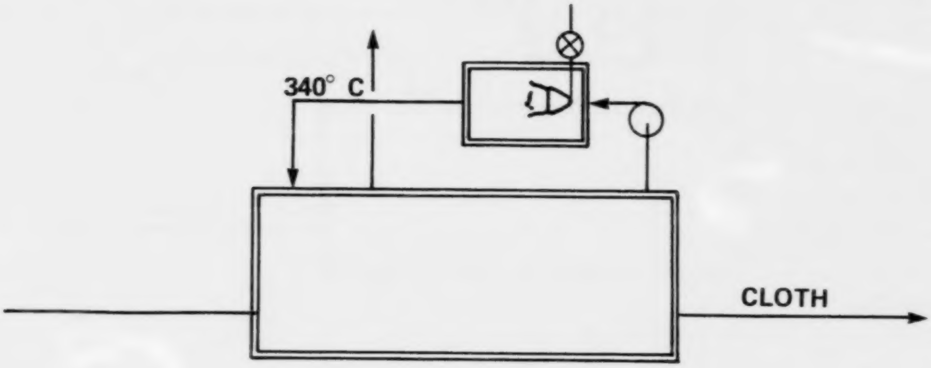


Figure 1. First incinerator category.

gases or elements, are subject to surface poisoning, which can permanently lessen their effectiveness.

In order of simplicity, there are about five different kinds of incineration systems for reducing the air pollution from textile dryers. The first incinerator category (Figure 1) removes air from the back end of a dryer, passes it through a combustor to heat it to 320° or 370° C, then reenters the incinerated stream into the drier front end. Since oil and resins evaporate at higher temperatures than water does, most of the smoke in textile dryers is created in the last zones of the dryer. This method destroys the smoke at the point of origin and has been reported to make a noticeable reduction of exhaust smoke. Actually, the exhaust from the dryer contains more smoke than the incinerated flow from the incinerator because the exhaust has whatever concentration exists inside the dryer. Any fuel used should be used on the exhaust stream leaving the dryer, thus obtaining maximum cleaning effect on the stream going to the atmosphere.

The second incinerator category (Figure 2A), often called an afterburner, takes air to be exhausted from the dryer, passes it through an incinerating combustor which heats it to 320° to 370° C, then either exhausts the incinerated stream directly to the atmosphere or passes it through a heat exchanger to recover some of the heat energy before exhausting. A variation of this, using the combustor of an indirectly fired dryer as the exhaust incinerator (Figure 2B), ran successfully in Mexico in 1974. The afterburner concept uses the presence of flames rather than high temperature to accomplish incineration.

The third incinerator category (Figure 3) and probably the most common in use in other industries has a heat exchanger before the incinerator to preheat exhaust air to be incinerated. High-temperature flow leaving the incinerator passes back through the hot side of the preheater exchanger to provide the preheat energy, and in so doing it gives up an equivalent amount of heat and is cooled. In essence the preheat heat exchanger makes it possible to raise the exhaust stream to higher temperatures, using less fuel to do so. Earlier it was mentioned that putting heat exchangers into the exhaust stream before the stream had been cleaned would cause dirt and smoke to soon plug the heat transfer surfaces. In this application, that is not so, because the heat exchanger is hotter than the exhaust gases; it is being used to heat, not cool, the exhaust stream. Oils, resins, and smoke will not condense on it. If the transfer surfaces are designed to pass lint on to the incinerator it will not require cleaning maintenance. The incinerated exhaust stream leaving the preheater-incinerator combination is still very hot and usually is passed through a heat recovery exchanger

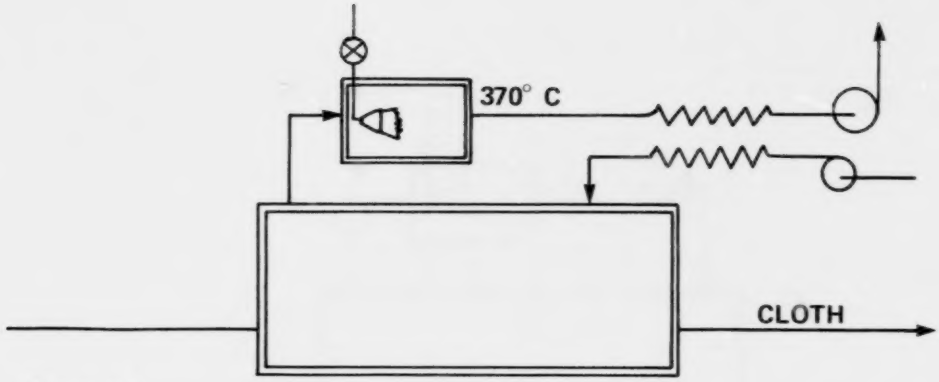


Figure 2A

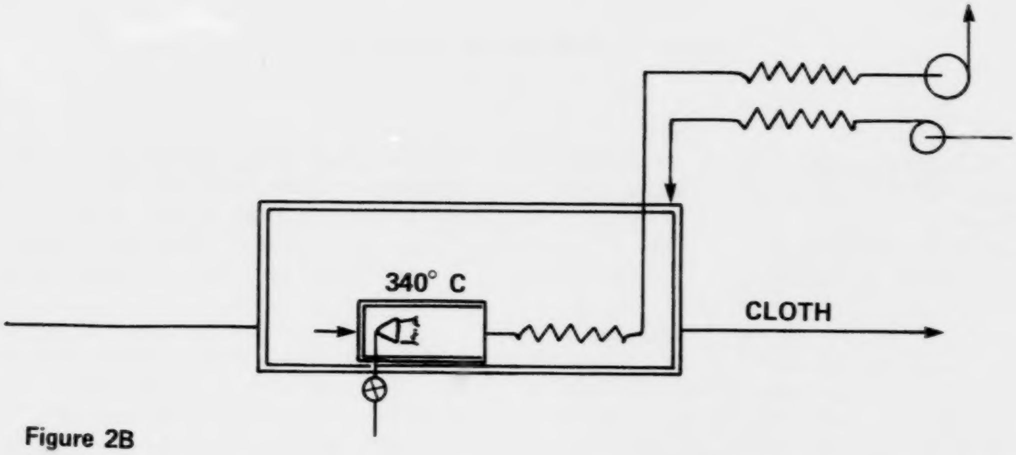


Figure 2B

Figure 2. Second incinerator category.

before exhausting to the atmosphere. With this system the first heat exchanger, the preheater, is most often a shell and tube arrangement. Incinerator chamber temperatures will probably exceed 450° C with this system; it does a good job of cleaning the exhaust stream, and, if enough heat exchanger surface is used for heat recovery to dryer makeup air, it can save 10 to 15 percent of the finishing process fuel bill.

The fourth incinerator category (Figures 4A and 4B) uses a recycling loop to pass dryer exhaust through a flame field a number of times before exhausting to recovery heat exchangers and the atmosphere. The recycle principle was first tried in 1974 on a modified indirect-fired dryer (Figure 4A) using the burners in the dryer as exhaust incinerators. The unit has been in continuous production since then in compliance with North Carolina code, and fuel savings exceed 60 percent. The recycle loop type incinerator (Figure 4B) incinerates at temperatures of 320° to 340° C with retention times of 2 seconds or longer. Retention is not as important as flame front exposure with a thin flat flame spread as wide as possible across the flow. The recycle duct carries hot gases back to premix with entering dryer ex-

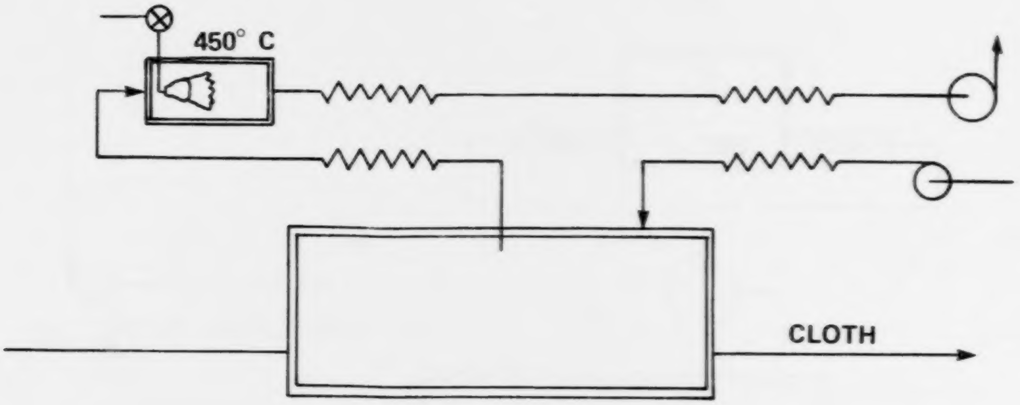


Figure 3. Third incinerator category.

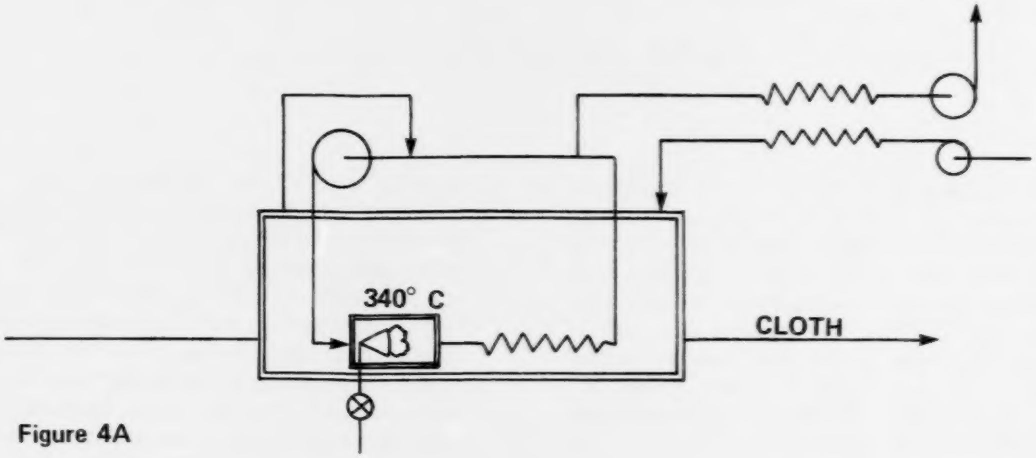


Figure 4A

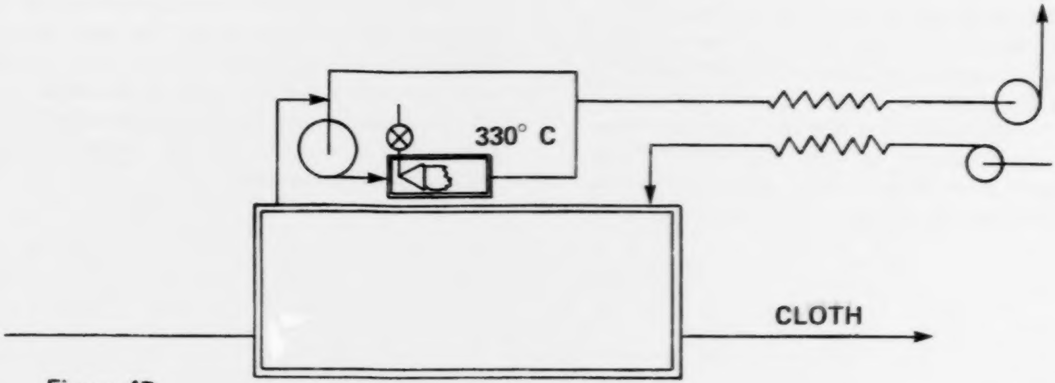


Figure 4B

Figure 4. Fourth incinerator category.

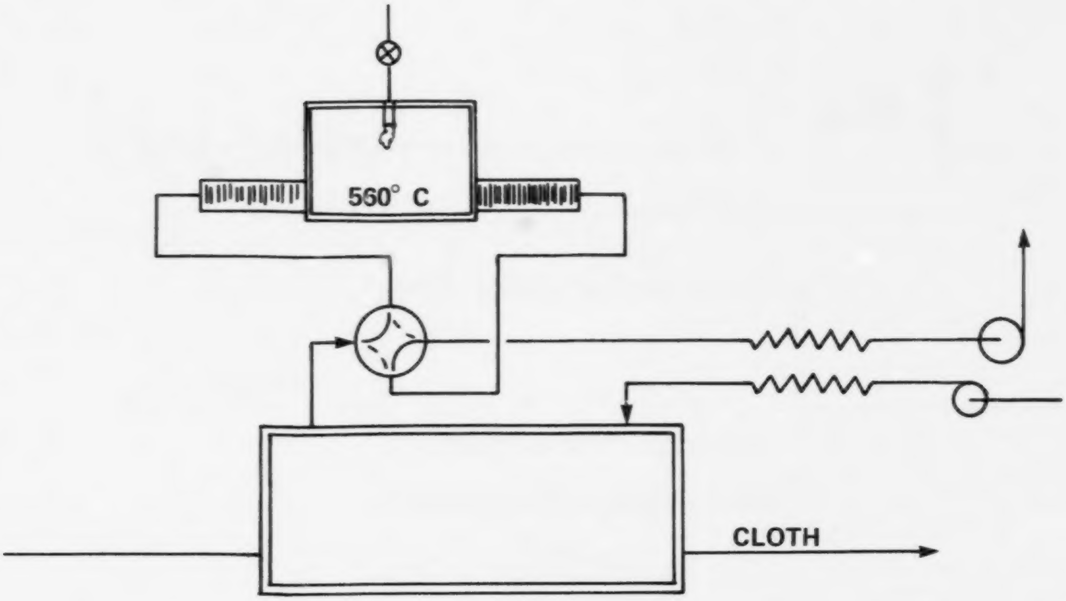


Figure 5. Fifth incinerator category.

haust. The mixing of hot and cooler gas acts as a preheater to preheat dryer exhaust to temperatures around 260°C before entering the combustor. The system uses a recovery heat exchanger to heat makeup air for the dryer to about 260°C. This hot makeup air carries enough heat back to the dryer to allow dryer operation with all of its burners turned off. Depending on the installation, fuel savings can run from 20 to 50 percent.

The fifth incinerator category (Figure 5) utilizes a high efficiency heat exchanger, 80 to 90 percent, to preheat exhaust to about 560°C before entering the incinerating chamber. The incinerating chamber has sufficient volume to hold the flow for about one-half second at 650°C. The method of heating from the entering temperature to the incinerator temperature is not important for incineration; that is, exposure to flame is not necessary. For practical design, the preheating heat exchanger should be a regenerating type. The regenerating exchanger reverses hot and cold flow over heat-storage elements. The system is very efficient, but 650°C temperature levels require construction with expensive high-temperature materials: ceramics for heat storage and refractory lining in the incinerator. Textile dryer exhausts contain many hydrocarbons which thermally ignite at temperatures below 540°C, probably all of them or what is left is of such small quantity to be of no consequence. It is very likely that 540°C peak levels will do an adequate job of incineration. The costs of construction materials for 650°C are very expensive compared to the cost of materials for 540°C. Again we are back to the point of doing that which is practical for the overall ecology with available resources.

FIXED BED CARBON ADSORPTION FOR CONTROL OF ORGANIC EMISSIONS

W. Macon Sheppard*

Abstract

Activated carbon processes have long been used for solvent recovery; however, these processes and variations of them are receiving increased attention for organics considered to be air pollution problems requiring emission control. In addition to the air pollution aspects, many recovery schemes previously labeled as uneconomical are now undergoing reconsideration due to increasing chemical costs. Activated carbon is one of several operations that can be employed to reduce organic emissions and in many cases recover valuable material or heat value.

When selecting the appropriate type of pollution control process, the physical properties of the contaminant and the level and frequency of emission can be used to determine whether the pollutant can be discarded, incinerated for heat value, or recovered as product. By concentrating emission streams, activated carbon can be used to produce fuels suitable for incineration, thereby increasing pollution control with reduced energy drain.

In designing fixed bed adsorption systems, pilot scale studies are the best method of obtaining the required design information. The most important factors to be evaluated are the breakthrough time, the length of the mass transfer zone, and the required regeneration cycle necessary to sustain an adequate carbon working capacity. Overall design considerations are governed by the required control efficiency and the available plant facilities.

INTRODUCTION

Some States are imposing, in State Implementations Plans, stricter limitations on organic emissions from stationary sources in order to meet Federal requirements for controlling ozone. Also, for the first time many States are beginning to require emission inventories on organics.

The most important regulatory action concerning organics is the increased attention being placed on carcinogenic compounds. The ruling of vinyl chloride as a hazardous substance due to increased incidents of angiosarcoma among workers was the first of what will surely be many organic compounds to undergo reduced emission levels and strict enforcement action. Since the vinyl chloride ruling, benzene has now been singled out as a health hazard and others are sure to follow. As in the case of vinyl chloride, strict emission limits set for health reasons will not be lowered due to complaints of poor economics or shortages of energy and technology. These emission limits, imposed by either State, EPA, or OSHA regulations, will be required of those industries where the specified organic is emitted from stacks, vents, or fugitive sources.

In addition to the air pollution aspects, increased attention is also being given to many recovery schemes previously labeled uneconomical, but now undergoing reconsideration due to increasing chemical costs. Activated carbon is one of several operations that can be employed to reduce organic emissions, and in many cases recover valuable material or heat value.

THEORY OF ADSORPTION

Adsorption is a process involving the concentration of materials at a surface or interface, whereas in absorption, the material goes into solution. Adsorption is normally thought of as a liquid or gas adhering to the surface of a solid; such as activated carbon. Such a material can either be physically or chemically adsorbed. Physical adsorption is the result of intermolecular forces of attraction between molecules of the solid and the substance being adsorbed. The adsorbed substance does not penetrate the lattice structure, but remains at the surface. The phenomena is reversible with an increase in temperature or a decrease in pressure removing the adsorbate in an unchanged form. In almost all cases, organics are physically adsorbed on activated carbon. Chemical adsorption (chemisorption) is a chemical reaction between the solid and adsorbate with the formation of bonds much greater than the forces of physical adsorption. This phenomena is frequently irreversible; e.g., oxygen chemisorbed on carbon is desorbed as CO or CO_2 (ref. 1).

---

*Environmental consultant.

The amount of a given material that will adsorb on activated carbon is most commonly determined by static equilibrium tests. The carbon is contacted with a given concentration at a constant temperature, and after equilibrium is attained, the mass increase of the carbon is measured. From these tests adsorption isotherms are formed. A typical isotherm is shown in Figure 1 (ref. 2). The adsorption capacity increases with a decrease in temperature and an increase in concentration and as a general rule, a vapor is more readily adsorbed the higher the molecular weight and the lower the critical temperature.

FIXED BED OPERATION

Carbon adsorption systems normally employ fixed beds of activated carbon. As shown in Figure 1 (ref. 3), as the pollutant is adsorbed from the gas stream onto the bed, an adsorption zone is formed which moves through the bed at a velocity much slower than the gas velocity. The breakpoint (or breakthrough) is that time when the adsorption zone (or mass transfer zone) reaches the end of the bed, and the pollutant concentration of the bed effluent begins to increase. The effluent concentration increases with onstream time, and at complete bed saturation will equal the influent concentration. Static equilibrium measurements of adsorption isotherms indicate the amount of organic adsorbed at saturation, but these data are not good design parameters since the onstream time of a fixed bed system is normally terminated short of complete saturation, usually soon after the breakthrough occurs.

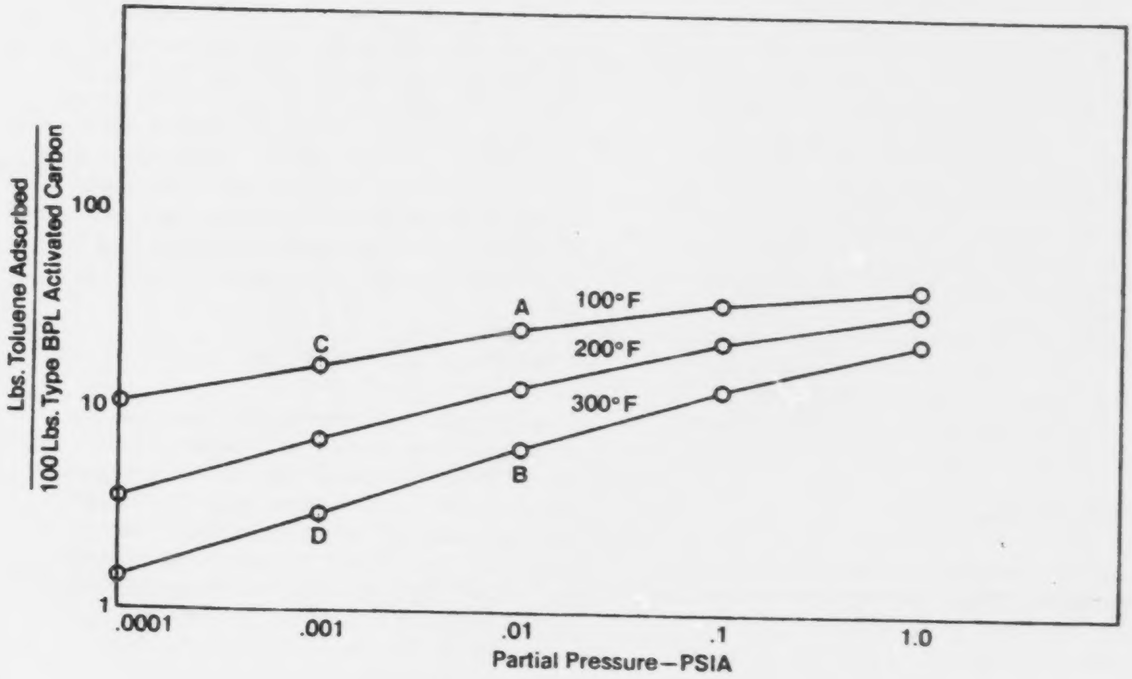


Figure 1. Toluene isotherms.

DESIGN CONSIDERATIONS

Pilot-scale studies are the best method of obtaining design information. Some factors that must be taken into account when designing an adsorption system and that can be evaluated in a pilot study are (ref. 4):

- *The breakpoint and shape of the breakthrough curve or length of the mass transfer zone.* Breakpoint times decrease with:
  - a decrease in bed depth,
  - an increase in carbon particle size,
  - an increase in flow rate, and
  - an increase in initial concentration.

  The length of the mass transfer zone is required to determine adequate bed depths (Figures 2 and 3). Normal bed depths are at least 2 to 3 times the length of the mass transfer zone. If the mass transfer zone is longer than the carbon bed, breakthrough is immediate.

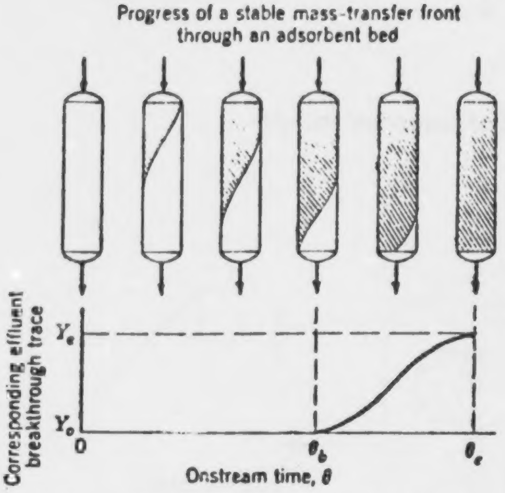

Progress of a stable mass-transfer front through an adsorbent bed
Corresponding effluent breakthrough trace
Y_e
Y_o
0
θ_b
θ_e
Onstream time, θ

Figure 2. Stable mass transfer front.

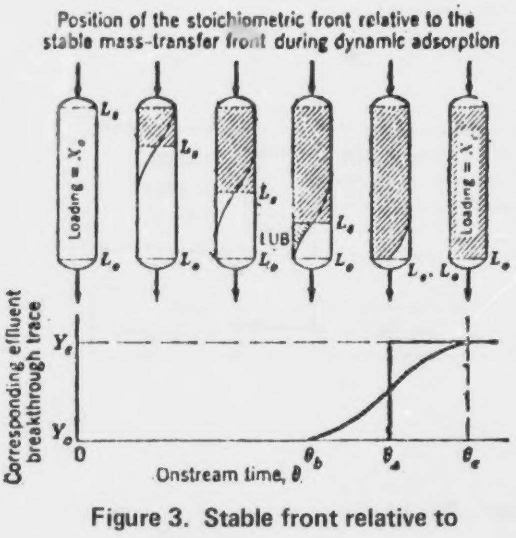

Position of the stoichiometric front relative to the stable mass-transfer front during dynamic adsorption
Loading = X_o
L_s
L_e
L_s
L_e
L_s
LUB
L_e
L_s
L_e
L_s, L_e
Loading = X_e
L_e
Corresponding effluent breakthrough trace
Y_e
Y_o
0
θ_b
θ_s
θ_e
Onstream time, θ

Figure 3. Stable front relative to stoichiometric front.

- *The working capacity of the carbon, at various temperatures, for the organic being removed from the stream.* The working capacity is the capacity restored by regeneration and cannot be determined from saturation capacities as shown in Figure 4 (ref. 4).
- *The pressure and flow rate of the stream being treated.* The pressure drop is required for determining bed depth and the particle size of the carbon to be used.
- *The desired and/or economical onstream time between regenerations.* Factors that may govern onstream time are:
  - minimum effluent concentration,
  - bed volume, and
  - regeneration time required to restore a desired working capacity.
- *The need for pretreatment of the pollutant stream prior to adsorption.* Pretreatment is sometimes necessary to remove heat, moisture, particulates, or aerosols (Figure 5).
- *The type of regeneration to be used.* Alternatives for regeneration are steam, air, vacuum, and thermal, as can be seen in Figure 5 (ref. 5).

POLLUTION CONTROL PROCESSES

Four general types of adsorption schemes can be defined as aids in selecting the appropriate type of control process (Figure 6). These are odor removal, pollution control, solvent recovery, and tank vent emission control (ref. 6).

Odor Removal (Figure 7)

Odor problems can occur when concentrations are less than 1 ppm, even though emis-

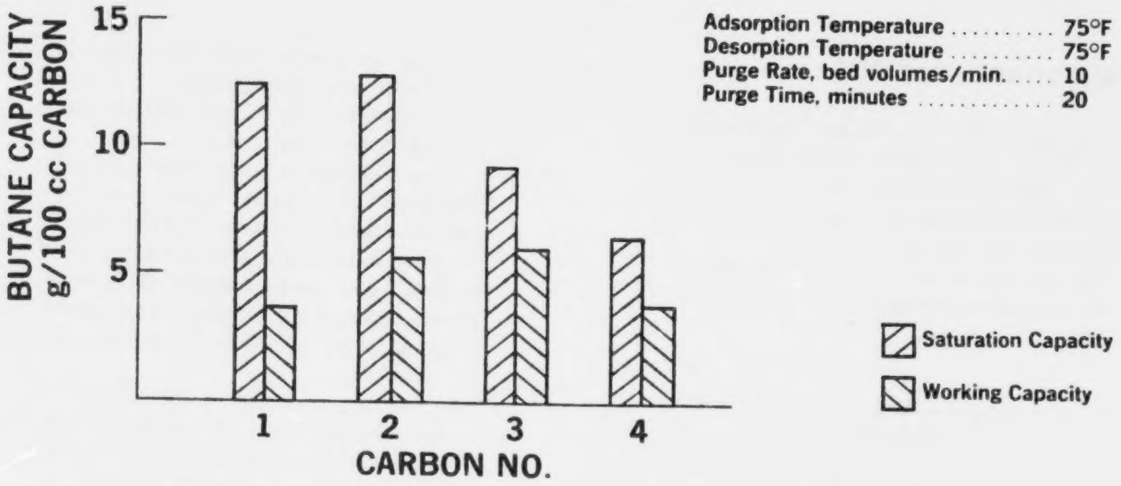


Figure 4. Working capacity is independent of saturation capacity.

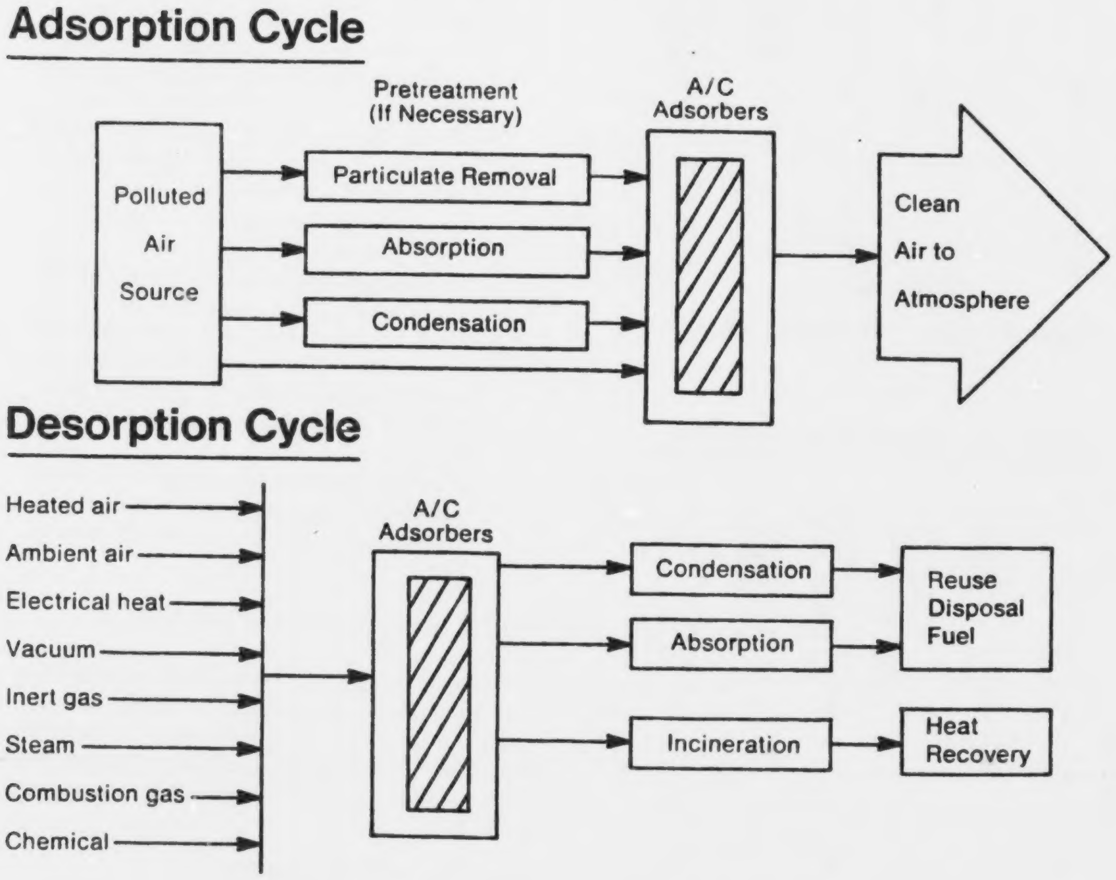
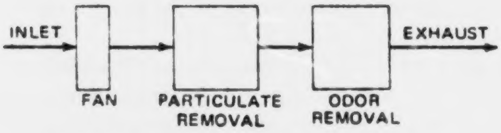

Adsorption Cycle
Pretreatment (If Necessary)
A/C Adsorbers
Polluted Air Source
Particulate Removal
Absorption
Condensation
Clean Air to Atmosphere
Desorption Cycle
Heated air
Ambient air
Electrical heat
Vacuum
Inert gas
Steam
Combustion gas
Chemical
A/C Adsorbers
Condensation
Absorption
Incineration
Reuse Disposal Fuel
Heat Recovery

Figure 5. Adsorption/desorption alternatives.

POLLUTION CONTROL PROCESSES

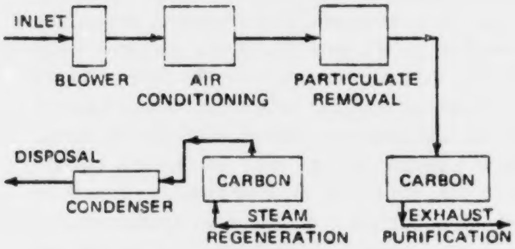
	Odor Removal	Pollution Control	Solvent Recovery	Tank Vent Emission Control
Concentration	1 ppm	1 ppm-0.1%	0.1%-3%	Various
Bed Depth (Typical)	1/2 in.	9 in.	24 in.	Various
Regeneration Method	Reactivate or discard	Regenerate in place	Steam Regeneration	Discard Carbon
Disposition of Collected Material	None	Incineration or disposal	Reuse	
Adsorption Cycle	1 year	1-8 hours	30-60 min	1-12 months

Figure 6. Pollution control processes.


INLET
EXHAUST
FAN
PARTICULATE REMOVAL
ODOR REMOVAL

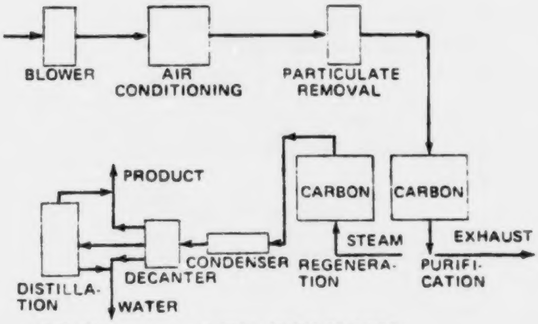
AIR FLOW - 2000 CFM/FILTER
PRESSURE DROP - 0.25" H_2O
CARBON LIFE - 1-2 YEARS
NEW FILTER COST - $220-$250
REACTIVATION COST - $ 80-$100

Figure 7. Odor removal system.


INLET
BLOWER
AIR CONDITIONING
PARTICULATE REMOVAL
DISPOSAL
CONDENSER
CARBON
STEAM REGENERATION
CARBON
EXHAUST PURIFICATION

AIR FLOW - 1000 - 100,000 CFM/BED
ADSORPTION - 1 - 8 HOURS
PRESSURE DROP - 10" - 20" H_2O

Figure 8. Pollution control system.


BLOWER
AIR CONDITIONING
PARTICULATE REMOVAL
PRODUCT
CARBON
CARBON
STEAM
EXHAUST
CONDENSER
DECANTER
REGENERATION
PURIFICATION
DISTILLATION
WATER

AIR FLOW – 1,000 – 40,000 CFM/BED
ADSORPTION – 30–60 MIN.
PRESSURE DROP – 20"–30" H_2O

Figure 9. Solvent recovery system.

sion quantities are minimal. In this system the air is filtered to remove particulates before being treated by the carbon. A thin bed of carbon or multiple sets of thin beds can be designed to handle large volumes of air and keep the contaminant below its threshold level for over a year. The spent carbon is then removed from the bed and either reactivated or discarded.

Pollution Control (Figure 8)

Emission problems where pollutant concentrations range from 1 to 1,000 ppm can be caused by odor or emission quantities. In this system, the stream may be filtered to remove particulates and/or cooled to increase adsorption. Normally, multiple beds are employed in cycles to allow one to be regenerated while another is undergoing adsorption. Economics normally dictate that the carbon be regenerated in place, but that the desorbed material not be recovered for reuse. Incineration is the normal disposal method.

Solvent Recovery (Figure 9)

A conventional solvent recovery system is usually employed when the pollutant concentration ranges from 1,000 ppm to the lower explosive limit. This system is the same as the pollution control system previously described, except that the large pollutant loadings require deeper beds even for short adsorption cycles, and organics are recovered for reuse in the regeneration cycle.

Tank Vent Emission Control (Figure 10)

In many cases the conventional solvent recovery process can be used to control emissions from tank vents; however, the process as described in Figure 10 is applicable where regeneration facilities such as steam or heat are not available. The process is simply a replaceable carbon bed which adsorbs vapor on tank filling and can be partially regenerated with inert gas as the tank is emptied.

The appropriate adsorption process can be selected based on the pollutant's physical properties, concentration, and emission frequency as shown in Figure 11. As a general rule, organics with a molecular weight below 30 are not adsorbed in quantities which make adsorption as practical as other control methods. Another factor is that with increasing boiling point, the pollutant is less readily desorbed from the carbon. Applicable systems are, therefore, those in which the carbon is not regenerated in place. Continuous operations are more conducive to cyclical adsorption systems with disposal or recovery based on the pollutant concentration in the stream.

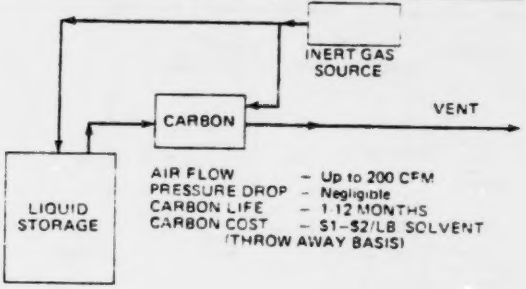

INERT GAS SOURCE
CARBON
VENT
LIQUID STORAGE
AIR FLOW – Up to 200 CFM
PRESSURE DROP – Negligible
CARBON LIFE – 1-12 MONTHS
CARBON COST – $1–$2/LB SOLVENT (THROW AWAY BASIS)

Figure 10. Tank vent emission control.

NOVEL ADSORPTION SYSTEMS

By concentrating emission streams, activated carbon can be used to produce fuels suitable for incineration, thereby increasing pollution control with reduced energy drain. In a typical solvent recovery unit, two beds are used to allow one to be regenerated with steam while the other is adsorbing solvent. Figure 12 illustrates a modification to this process in that the carbon is contained in annular beds at a depth of 4 inches. As steam is used to regenerate the beds countercurrently, concentrated airstreams containing steam can be sent directly to an incinerator (ref. 2).

Another adsorption system is used to concentrate a benzene emission stream from 85 ppm to 3,500 ppm, thereby reducing fuel requirements for subsequent incineration by a factor of 86 (ref. 2). As shown in Figure 13, the 85 ppm benzene stream is cooled to 150°F, then adsorbed on the carbon bed in an 8.5-h cycle. For regeneration a slip stream of the original 300°F emission is introduced to the carbon bed in a 4-h desorption cycle, which produces an effluent average concentration of 3,500 ppm. Whereas the 85 ppm stream would require 1,530,000 Btu's to incinerate at 1,400°F, the 3,500 ppm stream requires only 17,800 Btu's. A similar adsorption/incineration system patented as the Zorbcin Process (Figure 14) uses incinerator exhaust to desorb the carbon beds (ref. 7).

In addition to the commonly used solvent recovery process, recovery is also feasible with vacuum desorption. In such a system, the pressure is reduced below the partial pressure of the adsorbed organic material. The organic is then removed from the carbon in concentrations as high as 90 percent, which makes condensation and recovery attractive. A vacuum desorption system has been shown to be a viable method for controlling emissions from gasoline vapors during refueling operations. As shown in Figure 15, vapor concentrations of 10 percent to 40 percent are adsorbed and vacuum regenerated to 95 percent concentration levels (above the upper explosive limit). Although successful under these conditions, there is little data for vacuum desorption of dilute streams and low carbon loadings.

CRITERIA FOR SELECTION OF GAS CLEANING EQUIPMENT

Carbon adsorption is one of several operations that can be used to control organic emissions. Other techniques are adsorption by various liquid scrubbers and direct flame, thermal, and catalytic incineration. Criteria for selection of the proper processes are: desired collection efficiency, vapor stream characteristics, plant facilities and available utilities, and cost of control (Figure 16).

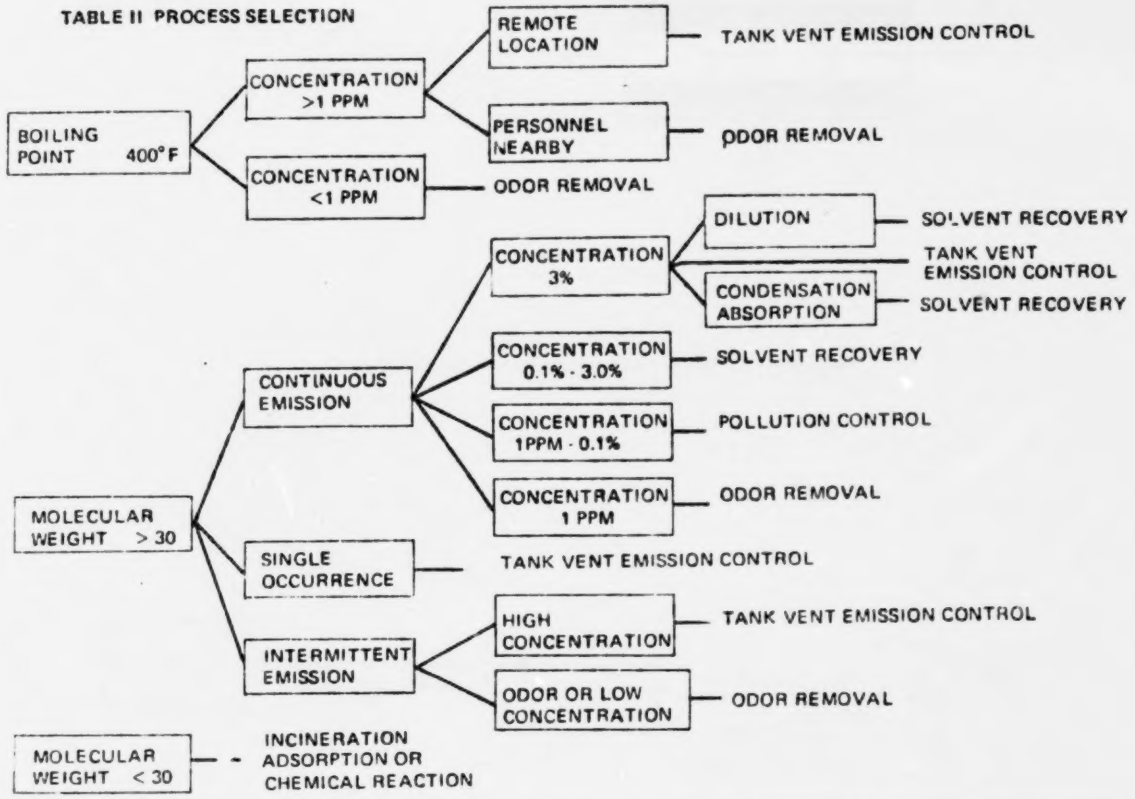


TABLE II PROCESS SELECTION
BOILING POINT 400°F
CONCENTRATION >1 PPM
REMOTE LOCATION
TANK VENT EMISSION CONTROL
PERSONNEL NEARBY
ODOR REMOVAL
CONCENTRATION <1 PPM
ODOR REMOVAL
MOLECULAR WEIGHT > 30
CONTINUOUS EMISSION
CONCENTRATION 3%
DILUTION
SOLVENT RECOVERY
TANK VENT EMISSION CONTROL
CONDENSATION ABSORPTION
SOLVENT RECOVERY
CONCENTRATION 0.1% - 3.0%
SOLVENT RECOVERY
CONCENTRATION 1PPM - 0.1%
POLLUTION CONTROL
CONCENTRATION 1 PPM
ODOR REMOVAL
SINGLE OCCURRENCE
TANK VENT EMISSION CONTROL
INTERMITTENT EMISSION
HIGH CONCENTRATION
TANK VENT EMISSION CONTROL
ODOR OR LOW CONCENTRATION
ODOR REMOVAL
MOLECULAR WEIGHT < 30
INCINERATION ADSORPTION OR CHEMICAL REACTION

Figure 11. Selection process for adsorption control.

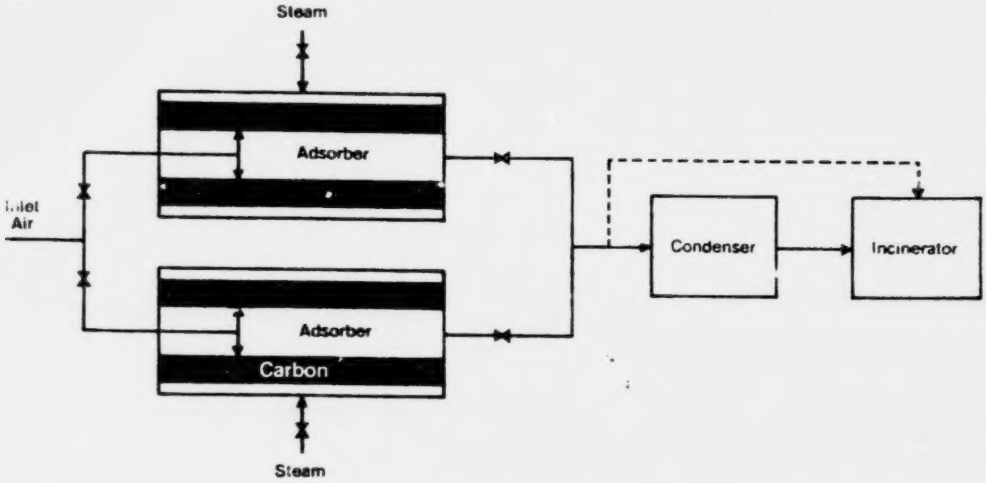

Steam
Adsorber
Inlet Air
Adsorber
Carbon
Steam
Condenser
Incinerator

Figure 12. Steam regeneration/incineration.

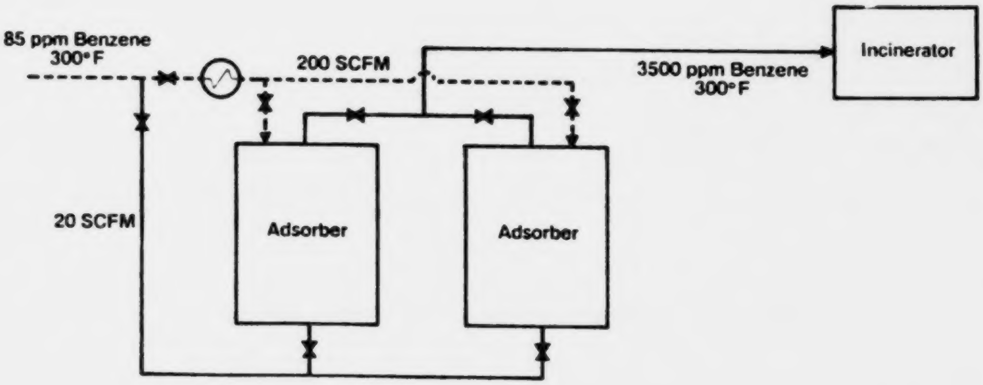

85 ppm Benzene
300°F
200 SCFM
Incinerator
3500 ppm Benzene
300°F
20 SCFM
Adsorber
Adsorber

Figure 13. Adsorption/incineration system.

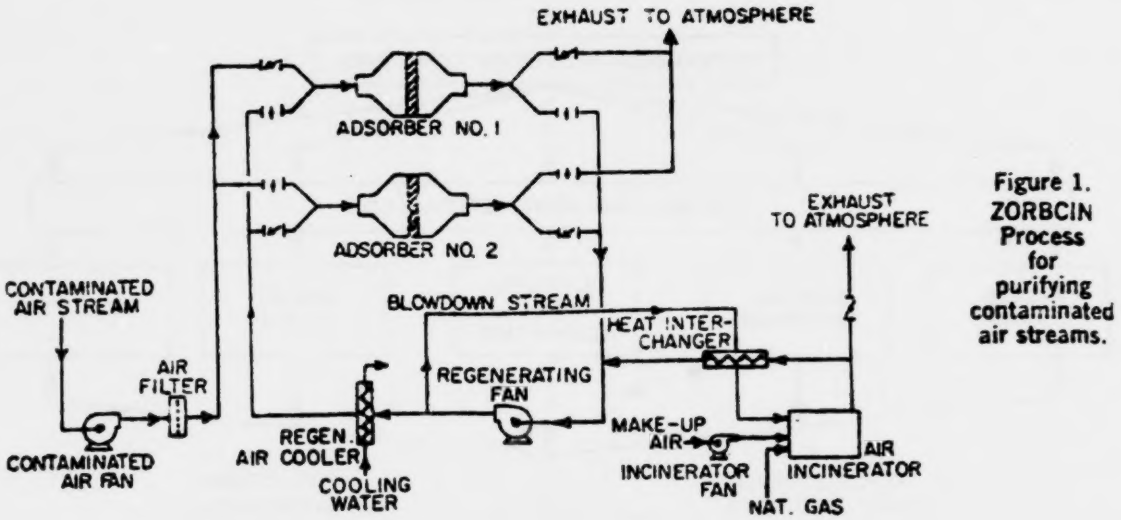

EXHAUST TO ATMOSPHERE
ADSORBER NO. 1
ADSORBER NO. 2
EXHAUST TO ATMOSPHERE
Figure 1. ZORBCIN Process for purifying contaminated air streams.
CONTAMINATED AIR STREAM
BLOWDOWN STREAM
HEAT INTER-CHANGER
AIR FILTER
REGENERATING FAN
REGEN. AIR COOLER
MAKE-UP AIR
AIR INCINERATOR
CONTAMINATED AIR FAN
COOLING WATER
INCINERATOR FAN
NAT. GAS

Figure 14. Zorbcin process.

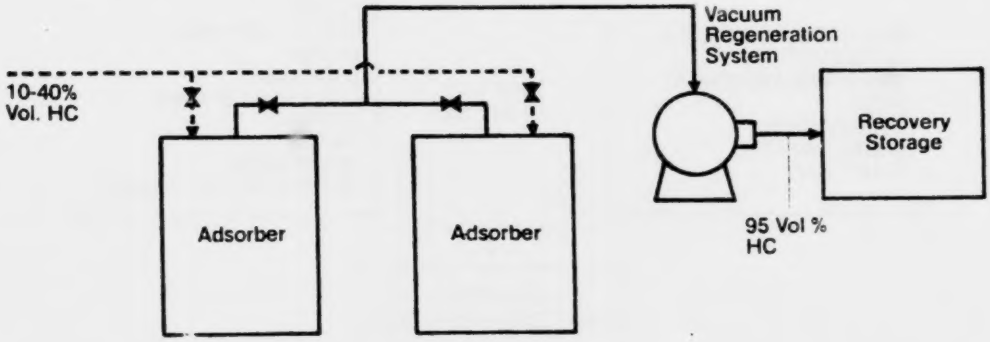

Vacuum Regeneration System
10-40% Vol. HC
Adsorber
Adsorber
Recovery Storage
95 Vol % HC

Figure 15. Gasoline vapor control system.

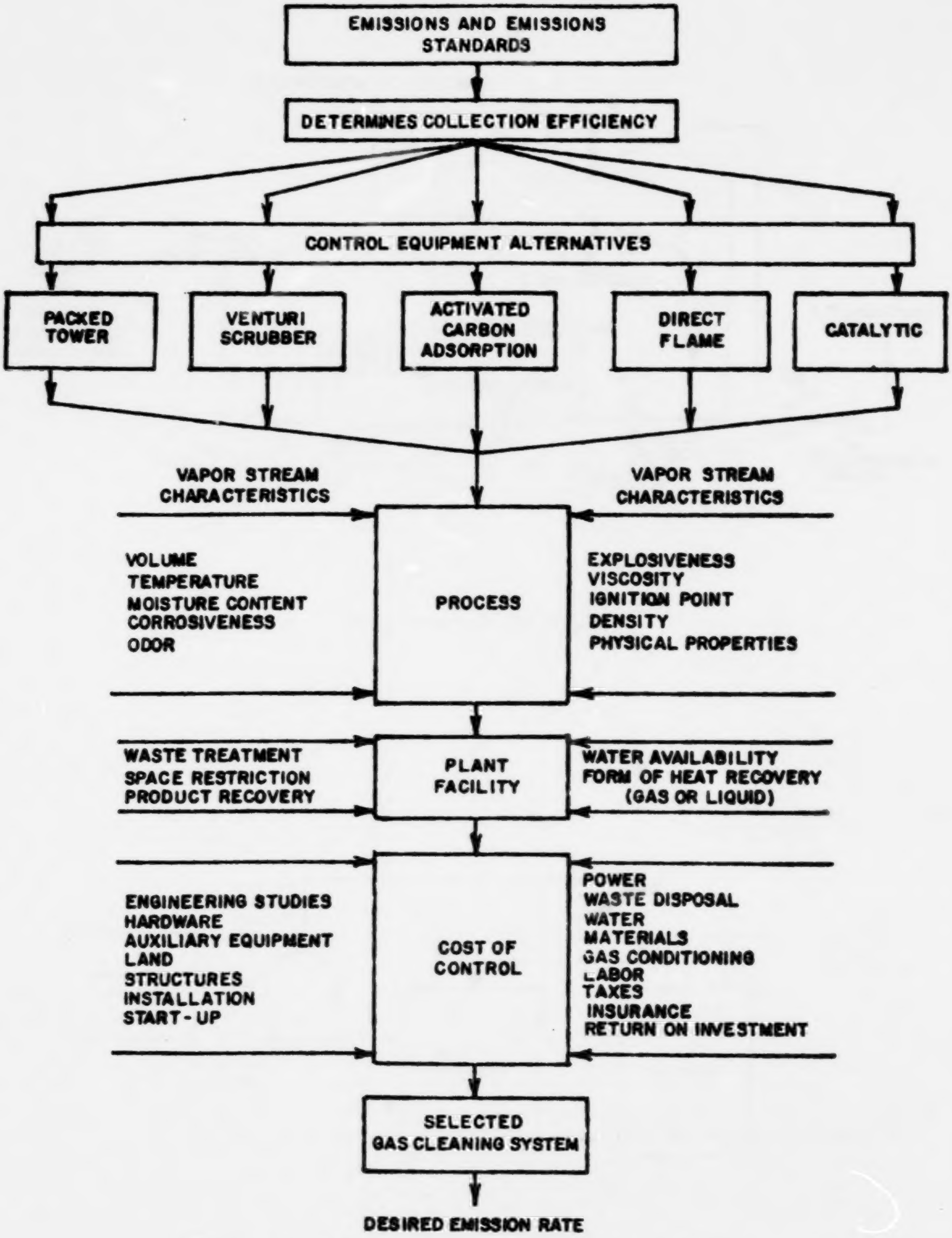

EMISSIONS AND EMISSIONS STANDARDS
DETERMINES COLLECTION EFFICIENCY
CONTROL EQUIPMENT ALTERNATIVES
PACKED TOWER
VENTURI SCRUBBER
ACTIVATED CARBON ADSORPTION
DIRECT FLAME
CATALYTIC
VAPOR STREAM CHARACTERISTICS
VAPOR STREAM CHARACTERISTICS
VOLUME
TEMPERATURE
MOISTURE CONTENT
CORROSIVENESS
ODOR
PROCESS
EXPLOSIVENESS
VISCOSITY
IGNITION POINT
DENSITY
PHYSICAL PROPERTIES
WASTE TREATMENT
SPACE RESTRICTION
PRODUCT RECOVERY
PLANT FACILITY
WATER AVAILABILITY
FORM OF HEAT RECOVERY (GAS OR LIQUID)
ENGINEERING STUDIES
HARDWARE
AUXILIARY EQUIPMENT
LAND
STRUCTURES
INSTALLATION
START - UP
COST OF CONTROL
POWER
WASTE DISPOSAL
WATER
MATERIALS
GAS CONDITIONING
LABOR
TAXES
INSURANCE
RETURN ON INVESTMENT
SELECTED GAS CLEANING SYSTEM
DESIRED EMISSION RATE

Figure 16. Criteria for selection of gas cleaning equipment.

REFERENCES

1. W. M. Sheppard, "A Study of the Steam Regeneration of a Fixed Bed of Activated Carbon Used to Adsorb Hydrogen Sulfide," Master's Thesis, Clemson University, 1970.
2. W. D. Lovett and F. T. Cunniff, "Activated Carbon Methods for Controlling Stationary Source Air Pollutants," presented at the Calgon Adsorption Conference, Pittsburgh, PA, 1975.
3. G. M. Lukchis, "Adsorption Systems," Union Carbide Corp. Pamphlet, reprinted from *Chemical Engineering,* 1973.
4. W. D. Faulkner, W. G. Shuliger, and J. E. Urbanic, "Odor Control Methods Using Granular ACtivated Carbon," presented at 74th National AIChE Meeting, New Orleans, 1973.
5. B. Grandjacques, "Air Pollution Control and Energy Savings With Carbon Adsorption Systems," Calgon Corporation Report No. APC 12-A, 1975.
6. J. C. Enneking, "Control of Vapor Emissions by Adsorption," ASHRAE Bulletin CH 73-2, 1973.
7. M. M. Mattia, "Processs for Solvent Pollution Control," *Chemical Engineering Progress,* Vol. 66, No. 12, 1970.

FLUIDIZED BED ACTIVATED CARBON ADSORPTION

Ram Chandrasekhar[*], Carmen M. Yon[†]

Abstract

Activated carbon adsorption and recovery of hydrocarbons has long been practiced in industry using fixed beds. With the development of special beaded carbon it is now possible to recover these hydrocarbons continuously in a fluidized bed. Fluidized beds are compact, easier to operate and maintain, and offer improved life cycle costs. PuraSiv® HR is a proprietary fluidized bed activated carbon adsorption/desorption system licensed by Union Carbide Corporation from Kureha Chemical Co., Ltd.[‡] *Details of the operation of fluidized bed activated carbon adsorbers, their application to textile plant exhausts, and relative merits over fixed beds are discussed in this paper.*

ACTIVATED CARBON ADSORPTION

The control of environmental pollution has become one of the industrialized world's major social goals. The textile industry is but one of many faced with a need for new technological innovations in dealing with the control of undesirable emissions. In the area of air pollution there are many opportunities for reducing the quantities of organic solvents, trace toxic substances, and malodorous compounds released to the atmosphere.

The processes that have emerged as the most successful in treating gaseous emissions are adsorption, absorption, incineration, and catalytic oxidation. Among these, only the first two offer the opportunity to recover substances for subsequent reuse. Although highly effective, the latter two methods require the consumption of much more valuable fuel, especially in applications where the pollutant is at low ppm levels. The use of adsorption, principally with activated carbons, has gained wide acceptance due to its versatility in removing a wide range of pollutants, its effectiveness of low concentrations, and its ability to yield a concentrated recovered substance for reuse.

Currently, nearly all activated carbon systems are of the fixed bed type. Granular or pelleted activated carbon of the desired size is packed in a vessel through which the solvent- (or pollutant-) laden gas is passed to effect removal. At some point before the activated carbon's adsorptive capacity is exhausted, the contaminated airstream must be switched to another vessel containing a bed of regenerated adsorbent. Steam is then passed through the spent bed of carbon to heat the adsorbent and strip the contaminant. In the case of solvent recovery the steam-vapor mixture goes to heat exchanger where it is condensed. If the solvent and water are immiscible, the two phases are separated in a decanter and each is further refined as necessary. If the solvent is miscible with water the stream must go to distillation in order to achieve a separation. For applications where recovery of the contaminant is not desired, the steam-vapor mixture can be incinerated since it is now more economically feasible due to the much higher fuel value of the stream. After the activated carbon has been regenerated, a stream of cool air is passed through the bed to cool and dry the adsorbent, preparatory to using it again for adsorption.

There are several limitations and disadvantages to the use of fixed beds. When a large volume of gas is to be treated, adsorption efficiency drops off due to the difficulty in obtaining uniform flow distribution across the face of the bed. In order to minimize the pressure drop across the bed (and thus power consumption), the adsorbent layer is usually very thin, sometimes only a few inches. Unfortunately, this leads to very poor utilization of the volume within a vessel and subsequent increase in equipment costs. In cases where high concentrations in the air must be treated, the heat generated by adsorption cannot easily be removed. Other problems arise from the batchwise nature of fixed beds. Each vessel must

---

[*] Foster-Miller Associates, Inc., Waltham, MA.

[†] Union Carbide Corporation, Tarrytown, NY.

[‡] Carbon Products Department (formerly Taiyo Kaken Co., Ltd.).

Preceding page blank

have several valves in order to properly sequence through the cycle steps: adsorption, desorption, cooling, and drying. These valves lead to leakage, operating, and maintenance problems. The containment of the activated carbon in a steel vessel requires that the metal as well as the adsorbent be heated up and cooled down every cycle. This results in an unnecessary use of utilities. When adsorption is carried out in fixed beds, there is always a portion of the bed that is not completely exhausted due to mass transfer resistance. This unused bed must still be regenerated each cycle, however, and this leads to increased utility requirements. The use of steam as the direct heating and desorbing medium leads to more difficult solvent recovery steps than if water were not present. The condensed steam can also present a very bothersome water pollution problem. Some years ago it became apparent that a continuous process based on fluidized bed adsorption offered a means of improving upon activated carbon adsorption.

FLUIDIZED BED ADSORPTION

If a bed of activated carbon is maintained in a fluidized state, there are many advantageous properties of the system. Particles in a fluidized condition behave much like a liquid. This means that the regenerated carbon can be continuously brought into contact with the contaminated air and a portion of spent carbon constantly withdrawn. The result is that only a small quantity of adsorbent need be maintained in the adsorption zone and very low pressure drops are achievable. The fluidity allows the adsorption zone to be designed as a series of stages analagous to a distillation tower with activated carbon introduced countercurrent to the gas onto the top stage and withdrawn from a bottom stage. When the adsorption is staged in this manner, it is possible to completely exhaust every bit of adsorbent before it is regenerated and regeneration heat and stripping gas are conserved. Because the velocities of gas needed to fluidize a bed are much higher than those allowable in a fixed bed, the gas phase mass transfer resistance is drastically reduced. A considerable amount of heat is generated when solvent is adsorbed at high concentrations. Fluidized beds transfer the heat away well, preventing "hot spots" that have been implicated in fixed bed fires. The ability to move the carbon into and out of a desorption zone eliminates the need to cyclically heat and cool the vessel walls with the accompanying waste of energy. Several attempts to apply fluid bed adsorption principles had previously been attempted with very limited success.

In the early 1930's, there was an attempt to develop moving beds of activated carbon without success (refs. 1,2). Around 1950, Union Oil Company developed the Hypersorption moving bed process for the recovery of hydrocarbons from natural gas and for other hydrocarbon fractionations (refs. 3,4). It was not until the mid 1960's that Cortaulds, Ltd. developed a fluid bed adsorber for the recovery of carbon disulfide from air in a rayon fiber plant and applied it to several solvents (refs. 5,6,7). All of the processes were plagued by excessive losses of activated carbon due to breakage and attrition. The capital costs were high and there were economic disadvantages in scaledown. The other major difficulty was breakdown of mechanical equipment, primarily that associated with transporting the carbon from section to section. One reason was the erosive nature of the adsorbent on steel parts. The successful use of fluid bed adsorption had to wait for the introduction of a dramatically different activated carbon and the development of a new process system to take full advantage of that product's unique properties.

PURASIV® HR ADSORBENT

PuraSiv® HR is a proprietary fluidized bed activated carbon adsorption/desorption system licensed from Kureha Chemical Company, Ltd. and sold by Union Carbide Corporation in the United States and Canada (refs. 8,9,10,11). The adsorbent around which the system has evolved is a beaded activated carbon (BAC) which is produced by a patented forming process (ref. 12). The raw material for the BAC is a molten petroleum pitch. Being thermoplastic, the molten material can be formed into nearly perfect spheres (see Figure 1) by the action of surface tension. Since the spheres are still thermoplastic, oversize and undersize particles can be recycled, yielding as narrow a size distribution as is needed without expensive losses. The beads are then carbonized and steam activated

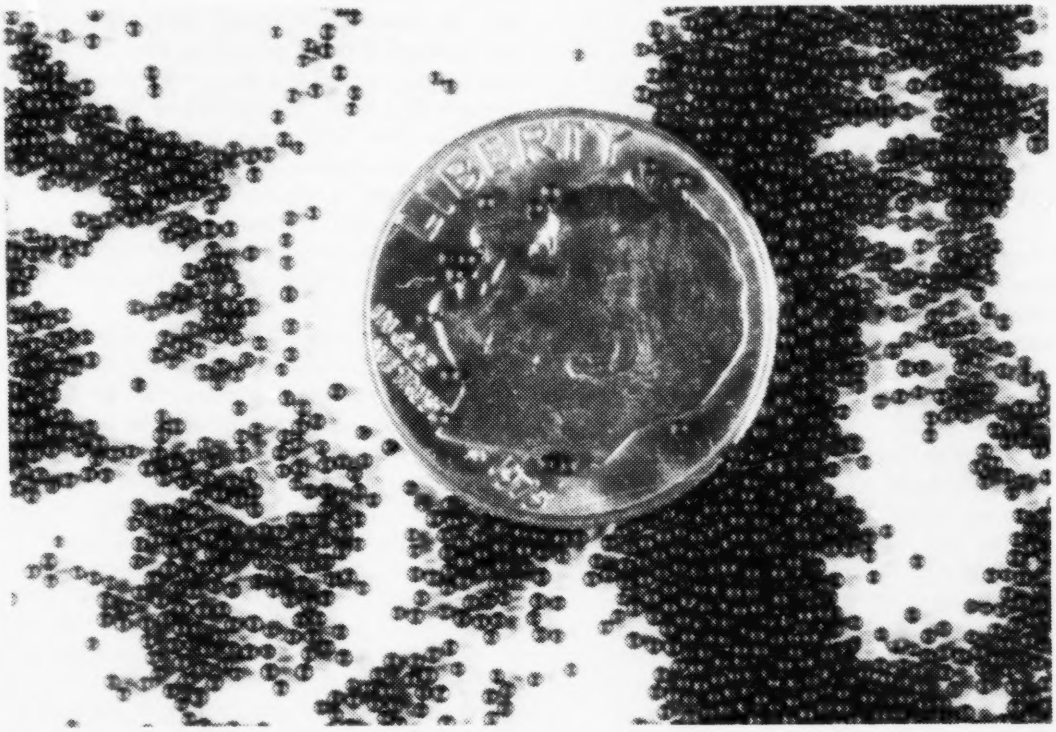


Figure 1. Beaded activated carbon.

under conditions similar to those used for conventional carbon activation. Careful control of the activation yields a PuraSiv® HR adsorbent with equilibrium loadings comparable to those of the highest grades of granular activated carbon.

The good mass transfer characteristics of BAC are attributable to its superior activation, very small size, and spherical shape. The combination of small size and spherical shape results in a high ratio of external surface area per unit volume, and this is conducive to high mass transfer rates. Also, the small diameter particles which characterize the PuraSiv® HR adsorbent have relatively small diffusion paths from the adsorbent surface to the adsorption sites and this results in higher diffusion rates. The activation given to the product results in a very large percentage of micropores in the range needed for solvent recovery. The resulting high pore volume and narrow pore size distribution also improve the mass transfer characteristics.

The fluidity of BAC, especially in the fluidized state, is nearly that of a liquid as would be expected from its particle shape. The sphericity and the narrow size distribution contribute to very stable fluidization and homogeneous flow patterns. This fluidity also allows for very easy transfer by a carrier gas and ease in charging and discharging of equipment. These same properties result in the ability to transport the BAC in a dense phase by gravity with little tendency to bridge in narrow passages.

Another result of the forming process is the excellent attrition resistance exhibited by the PuraSiv® HR adsorbent. As contrasted with products manufactured by binding powdery raw material or granulating nonhomogeneous substances, BAC has a structure that is uniform, homogeneous, and strong. This strength and the sphericity result in an adsorbent with attrition resistance that is significantly superior to conventional activated carbon. This higher attrition resistance not only reduces costs associated with adsorbent replacement, but also adds significantly to on-line operating time and minimizes particulate emissions.

All of these properties make BAC an ideal adsorbent for a fluidized bed adsorption process. It is around these unique qualities that the PuraSiv® HR process has been developed.

PURASIV® HR ADSORPTION SYSTEM

The heart of the PuraSiv® HR system is the adsorber/desorber vessel shown in Figure 2. The particular unit depicted is for a system utilizing nitrogen as the stripping gas and steam as the heating medium. There are many other means of stripping and heating that will be discussed later.

The adsorption section consists of multistaged fluidized beds. An important consideration is that the influent gas be introduced into the fluidizing section as uniformly as possible to insure uniform contact between the fluidized adsorbent and influent stream. The PuraSiv® HR system incorporates gas distribution structures which reduce impact pressure and allow proper distribution with a minimal pressure drop. Good gas distribution not only assures efficient adsorption but also eliminates "hot spots" believed to be one cause of fixed bed fires. The particles of adsorbent are fluidized by the upward moving gas and flow smoothly across the tray to the downcomers. The position of the downcomers are alternated on each tray, thereby eliminating dead space and allowing for uniform contact between the adsorbent and gas through the adsorption section. The gas velocities are several times those achievable in fixed beds and since there is only a single vessel the overall unit is more compact. The fluidized bed height is kept at a specified level by the weir. Particles from an upper stage fall onto a tray and overflow the weir into the downcomer. This patented tray design (ref. 8) results in efficient countercurrent contact of the PuraSiv® HR adsorbent with the upward moving gas. The adsorbent becomes progressively saturated with the solvent as it falls downward through successive trays of the adsorber and, after passing through the seal zone, falls into the secondary adsorption zone.

The purpose of the secondary adsorption section is to remove from the stripping nitrogen most of the residual solvent not condensed in the condenser. In this section the adsorbent falls as a dense moving bed countercurrent to the upward flowing stripping gas. The nitrogen leaving at the top has a solvent level low enough that it can be recycled as fresh desorption gas. The BAC has enough adsorptive capacity to accomplish this since the concentration of solvent in the nitrogen leaving the condenser is easily an order of magnitude higher than that in the adsorber. The adsorbent exits through another seal zone into the desorption section.

Desorption is usually carried out by raising the temperature and/or by reducing the partial pressure of the adsorbate (solvent that is adsorbed). This is often accomplished by desorbing with gases such as steam, nitrogen, or air, while simultaneously supplying sufficient heat to bring the material to the desired desorption temperature and to provide the heat of desorption. This heating can be accomplished directly or indirectly. In the PuraSiv® HR desorption section of Figure 2, the adsorbent, falling as a dense moving bed phase, is countercurrently contacted with the upward flowing stripping nitrogen. The heat of desorption is supplied indirectly by steam on the shell side of a shell and tube heat exchanger. The nitrogen for stripping is recycled from the secondary adsorber to the desorber bottom by a recycle blower. The solvent-laden stripping gas exits the top of the desorber to the condenser. Most of the solvent in the nitrogen is condensed and recovered while the nitrogen goes to the secondary adsorber. One of the advantages of using nitrogen in this recycle manner is that only a small amount of fresh nitrogen is required—that to make up losses. Since nitrogen does not condense as steam from a fixed bed would in the condenser, the condenser size and cooling water requirements are significantly reduced. The use of nitrogen allows solvents to be recovered with much lower water content, thus reducing the amount of post treatment before reuse. Because the steam for heating is applied indirectly, the steam condensate can be returned directly to the boiler system without expensive treatment to remove the dissolved solvent. In many cases with nitrogen stripping gas there will be no water condensate from the condenser to creat a secondary pollution problem.

After the BAC flows down to the bottom of

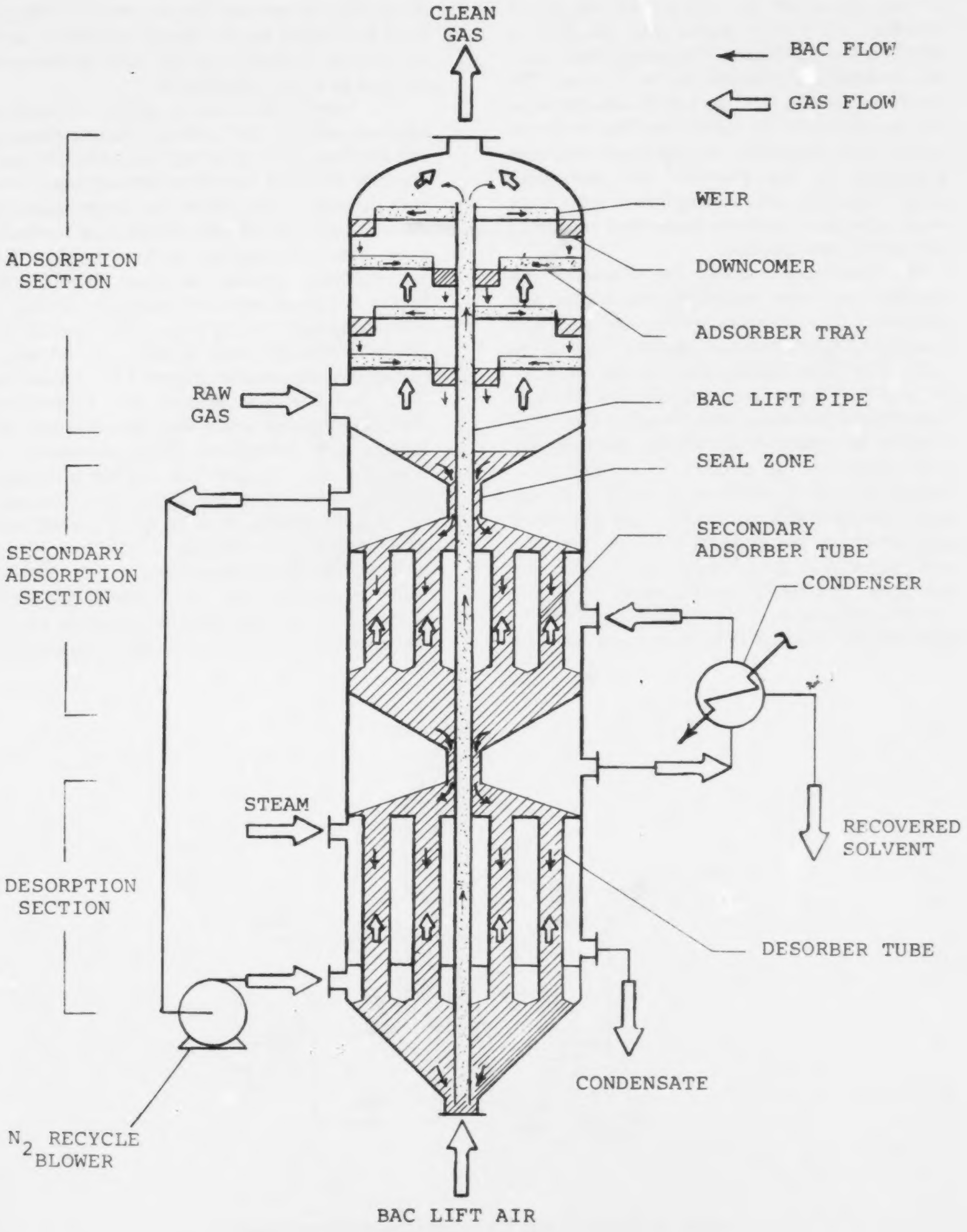

CLEAN GAS
BAC FLOW
GAS FLOW
ADSORPTION SECTION
WEIR
DOWNCOMER
ADSORBER TRAY
RAW GAS
BAC LIFT PIPE
SEAL ZONE
SECONDARY ADSORBER TUBE
SECONDARY ADSORPTION SECTION
CONDENSER
STEAM
RECOVERED SOLVENT
DESORPTION SECTION
DESORBER TUBE
CONDENSATE
N2 RECYCLE BLOWER
BAC LIFT AIR

Figure 2. PuraSiv® HR adsorber/desorber.

the column past the desorption section, it is recycled to the top of the adsorption section through the airlift line. The carbon and air are blended in a special nozzle and the BAC is lifted by the airstream. No mechanically moving devices are involved in the system. The airlift nozzle also acts as a seal zone between the desorber and the airlift line. Due to the excellent flow properties and attrition resistance possessed by the PuraSiv® HR absorbent, these transfers are accomplished with very small adsorbent attrition losses and relatively low power consumption.

As mentioned above, the PuraSiv® HR system has wide versatility in design and operation. The adsorber section can have any number of stages and any desired BAC-to-gas ratio. For some applications special formulations of BAC have been developed for difficult separations. However, the broadest flexibility is in the desorption section. Here the stripping gas and the heating medium can be custom designed for the application. In addition to the use of nitrogen discussed above, the desorbing gas can be air, steam, carbon dioxide, combustion gas, or fuel gas. Figure 3 illustrates the use of air for stripping perchloroethylene. The use of inexpensive air is possible for solvents that are not combustible. Steam can be used just as it is in conventional fixed beds. CO_2 and combustion gas would be used in the same way as nitrogen wherever they are more available. Fuel gas might be the choice for desorbing if the solvent or contaminant is to be incinerated or used as a fuel supplement.

The process also has a variety of heating means available. The indirect heating medium can be combustion gas, high temperature heat transfer fluids, or electric resistance heaters as well as steam. This allows the temperature of desorption to be selected for optimal performance. This is in contrast to fixed beds, which are generally limited to about 100°C. The higher temperatures are especially useful in recovering high boiling point materials and for deodorization applications to accomplish nearly complete desorption. Figure 4 is a schematic of a PuraSiv® HR system for recovering trichloroethylene, which uses direct steam for heating and desorption. Here, the steam is used directly because the trichloroethylene hydrolyzes with heat and moisture to form corrosive hydrochloric acid. To make a shell and tube desorber of material exotic enough to withstand such an environment can be prohibitively expensive. The use of direct steam requires only that the desorber walls be corrosion resistant and there can be a nonmetallic

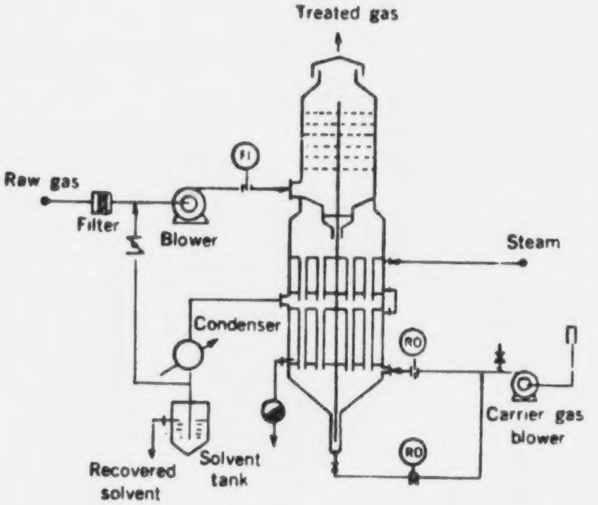


Figure 3. PuraSiv® HR for perchloroethylene recovery.

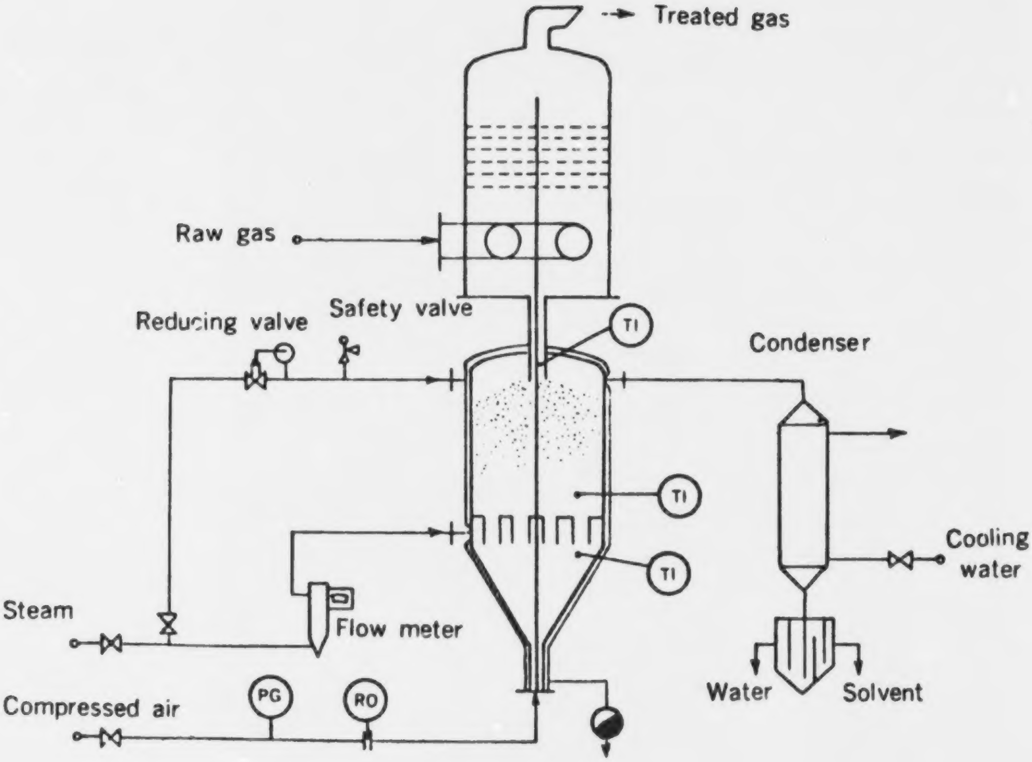


Figure 4. PuraSiv® HR for trichloroethylene recovery.

coating since there is no need for high heat transfer. Although the desorber is now similar to a fixed bed, the adsorber section still offers all of the fluidized bed advantages. Since the desorption section has a large impact on the capital and operating costs of the unit, the variations and flexibilities available in the PuraSiv® HR system allow an optimization of processing techniques and a minimum of costs.

The range of emission control problems that can be solved with this process are innumerable. Table 1 lists the solvents and contaminants that have been commercially treated by fluidized bed activated carbon adsorption. The range of applications treated include 6- to 4,000-nm^3/min flows and concentrations of 100 to 10,000 ppm by volume. A representative list of the commercial experience of the PuraSiv® HR system to date is shown in Table 2. Figure 5 is a photograph of one of these installations. The unit is used to recover an aromatic solvent from an adhesive coating vent stream. It is quite apparent that many of these, if not actually in textile finishing plants, are very closely related to the problems encountered there.

TABLE 1. FLUID BED APPLICATIONS

Acetone
Ammonia
Butyl alcohol
Carbon disulfide
Carbon tetrachloride
Ethyl acetate
Ethyl alcohol
Ethylene dichloride
Formaldehyde
Formalin
Isopropanol
Methyl cellosolve acetate
Methyl ethyl ketone
Naphtha
n-Hexane
Perchloroethylene
Phenol
Toluene
Trichloroethylene
Trimethyl benzene
Vinyl chloride
Xylene

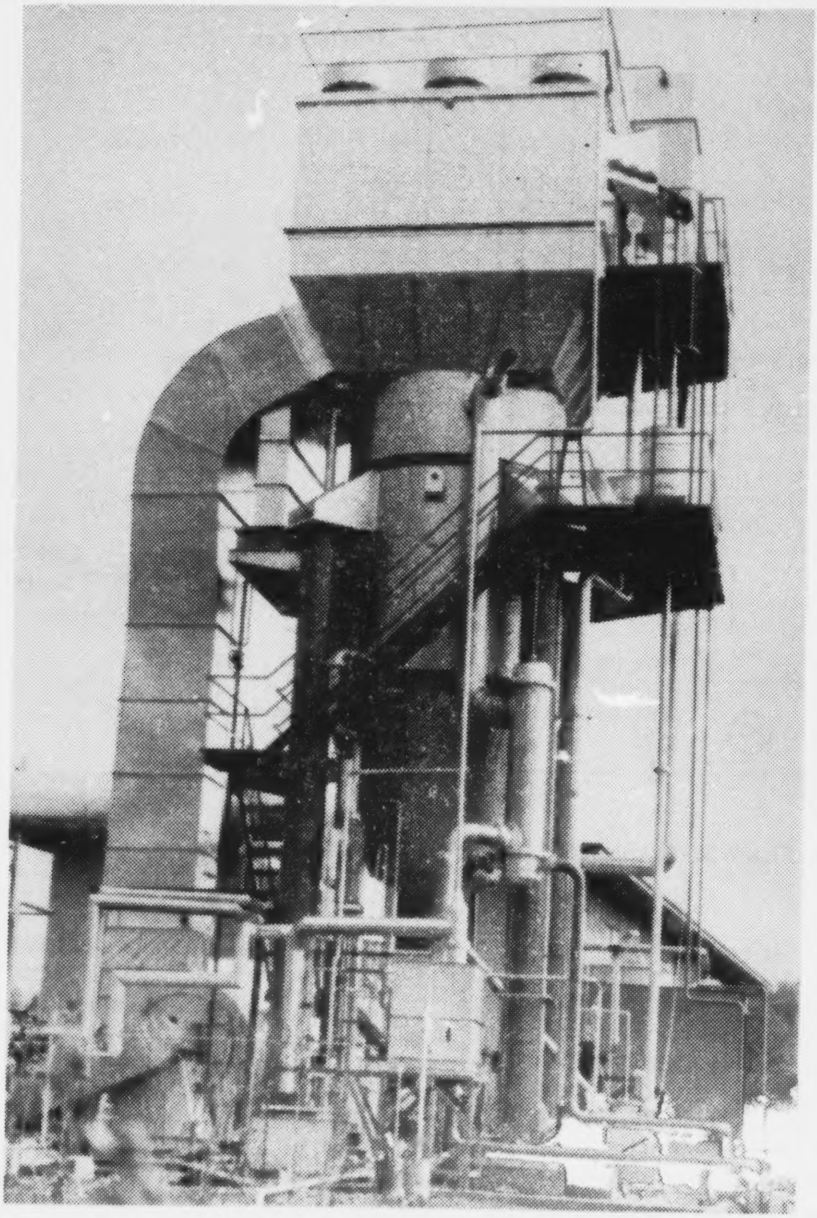


Figure 5. Commercial PuraSiv® HR unit (820 nm/min).

TABLE 2. PURASIV® HR COMMERCIAL EXPERIENCE

Application	Solvent	Flow (Nm^3/min)	Influent (ppm)	Effluent (ppm)
Cloth washing	Chlorinated solvent	20	4,600	30
Degreasing	Chlorinated solvent	30	3,500	50
Spray coating	Thinner	120	100	–
Chemical plant	Chlorinated solvent	50	3,560	70
Film coating	Aromatic solvent	250	1,680	30
Printing	Thinner	40	1,450	50
Degreasing	Mixed solvent	40	390	40
Printing	Aromatic solvent	180	1,800	80
Chemical plant	Alcohol	30	1,200	50
Degreasing	Chlorinated solvent	40	600	50
Adhesive coating	Aromatic solvent	820	2,710	50
Foundry	Odor	4,000	20	0.4
Lamination	Mixed solvent	120	2,000	50
Degreasing	Chlorinated solvent	50	1,500	50
Magnetic tape	Mixed solvent	200	2,800	50
Film coating	Aromatic solvent	100	1,000	100
Paper coating	Mixed solvent	200	550	80
Metal coating	Mixed solvent	300	2,800	100

APPLICATION OF TEXTILE PLANT EXHAUSTS

Use of activated carbon adsorption and/or solvent recovery from textile plant exhausts is complicated by the variety of fabrics and associated treatments involved. The fabric itself or the colors and patterns are changed very frequently. Common textile finishing operations include fabric preparation (including singeing, desizing, scouring, bleaching, and drying), printing/dyeing (including ageing, washing, and drying), and final finishing (application of special finishes and curing/heatsetting).

The principal variable in fabric preparation is the inclusion or exclusion of scouring and the need for chlorinated solvent scouring, as with some polyester fabrics, versus the use of water and detergents, as with most other fabrics.

In printing, combinations of certain dyes with acetate or acrylic fabrics causes emissions. Most other operations only evolve water vapor (ref. 13). If print pastes used with cotton or rayon fabrics include significant quantities of urea, again substantial emissions can be expected. In dyeing, the dye carriers change with colors used and fabric. All emissions occur during dye fixations (ageing).

The final finishing step basically involves the application of resins, most based on formaldehyde polymers, to bestow properties such as antistat, crease resistance and waterproofing, and heat setting the resin in a tenter frame at high temperatures. The resin formulations change with both the fabric as well as the kind of property imparted to the fabric.

The exhausts could be further diluted by area ventilations.

EFFECTS OF PROCESS VARIABLES

Various parameters significantly affect the performance of fluidized bed activated carbon adsorber. These include temperature, species of hydrocarbons and their concentrations, quantity of moisture present, and dust loading. The sizing of the adsorber, the choice of configurations, mode of desorption, materials of construction, and selection of ancillary equipment for pre- or post-treatment of the exhaust gases are highly dependent on these parameters as well as the presence of toxic or odorous compounds.

Activated carbon, in general, has greater affinity to higher molecular weight compounds and is effective with C_4 to C_{14} (boiling points in the range 65° C [149° F]/176° C [349° F]) species. Changes in adsorber/desorber are required beyond this range, for example, higher boiling organics will increase the severity of desorption. Certain chlorinated compounds break down forming inorganic acids necessitating proper selection of materials of construction.

The adsorption of hydrocarbons by activated carbon is concentration dependent at a given temperature. Hence, lower inlet concentrations will require more severe desorption to achieve a preset degree of emission control.

Textile plant exhaust temperature approaches or exceeds normal desorption temperature of activated carbon. These gases, therefore, will require precooling prior to entering the adsorber. The degree of precooling usually prescribed can easily be carried out either with tower cooling water or with gas/gas heat exchangers depending on the reuse economics of the recovered heat. Close attention will have to be paid to undesirable condensation of vapors in the heat exchanger. Lower inlet concentrations may require lower inlet temperatures if the hydrocarbon recovery required is a very high percentage of the inlet concentration.

Relative humidities of up to 50 percent at 38°C (100°F) have been easily handled in carbon bed adsorbers. Depending on the mode of desorption, products end up with 2 to 20 percent water. Higher moisture content of the exhaust gases result in more water in the product. Special dehumidification may be required if the humidity far exceeds 50 percent.

Dust, in finishing plants, appears in the form of lint. Unless sticky or rendered sticky prior to entering the adsorber and likely to clog the distributor plates, the system will allow dust to pass right through without affecting performance.

Levels of toxic and odorous hydrocarbons permitted in the exhaust gases are usually lower than those for other hydrocarbons. Often, the inlet concentrations are also low. If it is not possible to adsorb them along with the rest of the hydrocarbons, a separate finishing stage is added to the fluidized bed and the activated carbon stream is handled separately with more severe desorption conditions and the desorbed gases are usually incinerated to render them innocuous using less fuel than if

TABLE 3. APPLICATION EXAMPLES OF FLUIDIZED BED ADSORBERS

Solvent	Perchloroethylene	Trichloroethylene	Toluene
Inlet gas			
Flow rate (nm^3/min)	15	9.3	240
Temperature (° C)	40	20	47
Concentration (ppm/vol)	4,600	2,600	1,680
Outlet gas			
Concentration (ppm/vol)	30-40	20-30	<50
Desorption			
Gas flow rate (nm^3/min)	$36^{(\text{air})}$	$47^{(\text{steam})}$	$80^{(N_2)}$
Temperature (° C)	145	110	160
Carbon			
Inventory (kg)	300	90	1,500
Circulation rate (kg/h)	120	30	600
Utilities			
Electricity (kwh)	37	2.3	22
Steam (kg/h)	20	50	100
Cooling water (ton/h)	0.6	1	3
Nitrogen (nm^3/h)	–	–	1.5
Solvent recovered (kg/h)	20	8	100

the incineration were carried out without adsorption/desorption.

PERFORMANCE CHARACTERISTICS OF FLUIDIZED BED

Table 3 illustrates the performance capabilities of some typical fluidized bed activated carbon adsorbers. It must be noted that these are not the performance limits.

Fluidized Bed Versus Fixed Bed

- Adsorption and desorption can be carried out continuously in a single vessel.
  - – There are no valves to be manipulated to switch vessels.
  - – The vessels are not alternately heated and cooled, only the carbon is, effecting significant energy savings.
- Capital and installation costs are lower because of the single vessel configuration, elimination of timers, valves, duplicate heating and cooling systems, emissions monitoring system to check bed saturation, etc., and smaller, compact equipment which results from high gas flow rates per unit area.
- Homogeneous fluidization and continuous flow of carbon avoids maldistribution of

TABLE 4. ECONOMICS OF FLUIDIZED BED ADSORBERS

Operating conditions	Case 1		Case 2	
Solvent	Toluene		Naphtha	
Inlet gas				
Flow rate (nm^3/min)	240		940	
Temperature (° C)	47		38	
Concentration (ppm)	1,680		105	
Outlet gas				
Concentration (ppm)	<50		<10	
Solvent recovery (kg/h)	100		26	
Operating time (h/yr)	8,000		8,000	
Costs	Fluidized bed	Fixed bed	Fluidized bed	Fixed bed
Equipment cost ($)	200,000	180,000	510,000	500,000
Installation cost ($)	50,000	75,000	130,000	200,000
Space requirements (m^2)	37	75	150	200
Utilities				
Steam (kg/h)	100	365	33	135
Electricity (kwh)	22	44	80	140
Cooling water (ton/h)	3	22	0.7	8
Nitrogen (nm^3/h)	15	–	0.25	–
Annual operating cost ($)	14,400	38,000	21,900	44,000
Annual maintenance cost ($)	8,000	15,000	20,000	40,000
Annual carbon replacement cost ($)	800	1,000	200	2,000
Payback period (yr)	2.1	2.9	–	–

gases improving adsorption efficiency.

- For the same reason above, hot spots are not formed, making fluidized beds less prone to fires.

Economics of Fluidized Bed Adsorbers

Table 4 shows cost comparisons for two different applications of fixed and fluidized bed activated carbon adsorbers.

CONCLUSIONS

With the advent of stronger, fluidizable activated carbon, fluidized bed carbon adsorption of hydrocarbon emission control and solvent recovery has become a reality and shows distinct advantages over traditional fixed bed operations. Maldistribution of gases, associated with fixed beds, is minimized resulting in the most efficient use of the carbon. Both hot spots created by nonuniform gas distribution and high bed temperatures, which result if the inlet solvent concentration is very high, are also eliminated. Design flexibilities permit fluidized beds to cope with ever-changing composition of exhaust gases from textile finishing plants. Compactness and continuous operation in a single vessel improve the overall economics of fluidized beds over fixed beds.

REFERENCES

1. V. Pantenburg, "Process for Regeneration of Adsorption Material," U.S. Patent 1,784,536, issued December 9, 1930.
2. F. J. Bechtold, "Regenerating Granular Adsorbents," U.S. Patent 1,836,301, issued December 15, 1931.
3. W. F. Bland, "Design Details, Operating Results of First Commercial Hypersorber," *Petroleum Processing*, July 1948.
4. C. Berg, "Hypersorption in Modern Gas Processing Plants," *Petroleum Refiner*, Vol. 30 (No. 9), September 1951.
5. H. M. Rowson, "Fluid Bed Adsorption of Carbon Disulfide," *British Chemical Engineering*, Vol. 8 (No. 3), March 1963.
6. D. A. Avery and D. H. Tracey, "The Application of Fluidized Beds of Activated Carbon to Solvent Recovery from Air or Gas Streams," Institution of Chemical Engineers Symposium Series No. 30, 1968.
7. D. A. Avery and D. A. Borston, "The Recovery of Solvents From Gaseous Effluents," *Chemical Engineer*, January/February, 1969.
8. H. Murakami, et al., "Method for the Purification of Waste Gas Containing Gaseous Pollutants," U.S. Patent 4,047,906, issued September 13, 1977.
9. H. Murakami, et al., "Method and Apparatus for the Purification of Waste Gas Containing Gaseous Pollutants," U.S. Patent 4,061,477, issued December 6, 1977.
10. Y. Sakaguchi, "Development of Solvent Recovery Technology Using Activated Carbon," *Chemical Economy & Engineering Review*, Vol. 8 (No. 12), December 1976.
11. Anon, "Beaded Carbon Ups Solvent Recovery," *Chemical Engineering*, Vol 84 (No 18), August 29, 1977.
12. Y. Amagi, et al., "Method for the Preparation of Carbon Moldings and Activated Carbon Moldings Therefrom," U.S. Patent 3,917,806, issued November 4, 1975.
13. H. H. Northup and W. F. Turner, "Air Pollution Control in Textile Finishing," Textile Chemist & Colorist, Vol. 7 (No. 4), April 1975.

CATALYTIC OXIDATION OF HYDROCARBON FUMES

Richard E. Githens, Donald M. Sowards*

Abstract

The efficiency of fixed-bed vapor/solids catalyst beds has been determined and correlations published to permit accurate design of catalyst beds. These designs have been used successfully in textile and other applications. All existing EPA guidelines can be met for the oxidation of hydrocarbon emissions if these design procedures are followed.

The operating costs for fuel are substantially less than for thermal incineration. Both thermal and catalytic afterburners utilize heat recovery, recirculation, and stack gas economizers in the design of systems.

INTRODUCTION

The utility of heterogeneous catalysis in air pollution control is well established in such fields as nitric acid manufacture, chemical plant emissions, and paint bake ovens. It has been equally successful, but less well known, in the textile fibers field. This article will discuss some of the applications of particular interest to the textile fibers industry.

DESIGN BASIS

There are many published reports on catalytic reactions in the gas phase using a solid catalyst. The manufacture of many chemicals is dependent upon a detailed knowledge of the reaction kinetics, heat and mass transfer, and pressure drop. Nitric acid, hydrogen cyanide, and formaldehyde are but a few of such commercial heterogeneous catalytic operations.

Less publicized, but equally well known to those in the field, are the design methods for oxidation of hydrocarbons to carbon dioxide and water (refs. 1,2 and Table 1). Each supplier of catalysts has his own research data and calculation methods but, for reference purposes, the report prepared by Shell Development Company for the U.S. Environmental Protection Agency will be used (ref. 3). Referring to Figure 1, it has been found that most of the practical commercial installations of catalytic afterburners are operated in the range of flow and temperature where mass transfer is controlling. There are at least six different forms for the catalyst substrate and as many catalyst compositions. For brevity, this paper will show correlations only for three substrates and a single precious metal catalyst (Figures 1 through 7).

A monolithic honeycomb structure made from various grades of alumina or other ceramics is one type of substrate. Cylindrical pellets (1/8 in. diameter × 1/8 in. high) are another type of substrate or support. The third is a wire mesh pad made of appropriate high-temperature metallic ribbon. All can be coated with platinum, palladium, or other precious metals. Not considered here are the various metal-oxide catalysts that are also used in some applications. Miller and Wilhoyte (ref. 2) showed that when the flow velocity and temperature are in the range where mass transfer is controlling, the honeycomb ceramic supports are more efficient than pellets or metal foil supports. Note that both pellet beds and metal-ribbon beds must be larger in diameter than honeycomb ceramic beds to run at the same pressure drop. This is important because the size of the catalyst bed affects the size and cost of the system containing the catalyst.

CAPITAL COST

Each system is custom designed and there are many variables that can affect the cost of the system. Consequently two systems with identical gas flow rates can have widely different costs. Some of the variables that have significant effects on cost are:

---

*E. I. du Pont de Nemours & Company, Inc.

- Type and efficiency of the heat exchanger, if used at all;
- Degree of complexity of the instrument control panel and the controls;
- The number and type of dampers used to control recirculation;
- The type of burner train used; and
- The amount and type of catalyst.

In spite of these differences, it seems useful to have some guidelines as to the relative cost versus the flow rate. Several recent examples from our sales files attempt to break them down into broad categories. (These are shown in Figure 5 as unit costs per SCFM versus flow rate in SCFM.)

- The main incinerator body including catalyst, plus all the blowers, burners, controls, and instruments.
- The recuperative heat exchanger and its associated duct work.

Limited personal experience with thermal oxidation systems indicates that the total cost of the system is very similar to the total cost for a catalytic oxidation system but the individual breakdown is, of course, different (refs. 3,4). The thermal system must be designed for higher operating temperatures.

The spread of our data around the curves shown is probably ± 20 percent due to the differences previously noted and should be indexed from June 1978.

OPERATING COST

The main advantage of a catalytic system versus a thermal system is the energy savings due to reduced fuel consumption (refs. 5,6,7). The catalyst replacement cost must be considered as an offset to the fuel savings. Although suppliers usually warrant the catalytic life for only 1 year, our experience in hydrocarbon applications is that the catalyst can last well beyond this with proper care and maintenance. A good average figure would be 4 years, but we have catalysts still in use after 6 years.

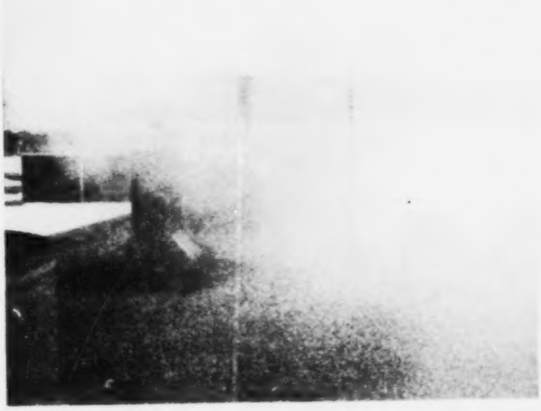
Examples chosen to illustrate the effect of solvent load on fuel consumption are shown in Tables 2, 3, and 4. At any concentration above about 5 percent of the lower explosive limit (LEL), the catalyst system can run self-sustaining and no fuel is required if a 70 percent effective heat exchanger is used. Above about 30 percent of the LEL, the solvent concentration will cause enough temperature rise that dilution must be used to prevent overheating of the catalyst. For high concentrations like this, it is freqently more economic to use thermal oxidation. However, in most textile operations we are operating catalytic abatement equipment well below 30 percent of the LEL. In most tenter frames the concentration is below 3 percent of the LEL.

INSTALLATION COST

For a typical textile plant installation, labor cost for tie-ins is about 40 man-days of time ($1.50/SCFM). However, each case must be determined individually because of site differences. All of the units up to 20,000 SCFM are skid-mounted on one skid and need only be connected to the duct work and utilities after mounting on the roof support steel. Above 20,000 SCFM, the units may be on one skid or may be broken into two or more skids for ease of shipping. In this case, the pieces may be mounted on the roof and then connected by field contractors (Photographs 6, 7, and 8).

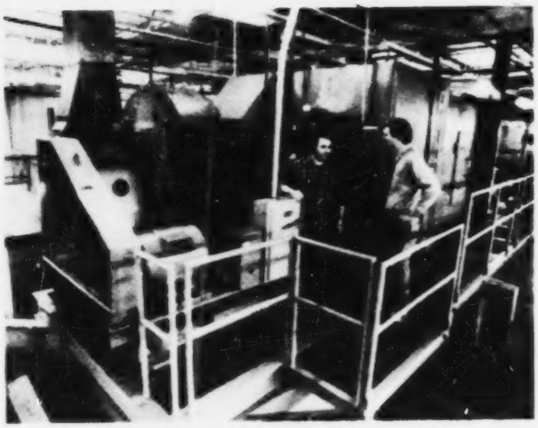
EXAMPLES OF EXISTING INSTALLATIONS OF CATALYTIC AFTERBURNERS

- A printworks in New England using a Thermosol oven to cure polyester/cotton printed fabric had problems with visibility and odor complaints from residents. A catalytic incinerator was installed, which solved these problems. Approximately 80 percent of the clean, hot air is recycled to the oven. The net reduction in fuel costs was approximately $5,000/yr at 1976 fuel values. A thermal incinerator required to do the same job was more expensive and would have consumed far more fuel. The plant engineer stated that the catalytic reactor "is the only control system I saw that is not energy intensive — the only one that does not require more energy than we normally use in our printing operation." (See Photograph 5.)
- A finishing plant in southern Penn-

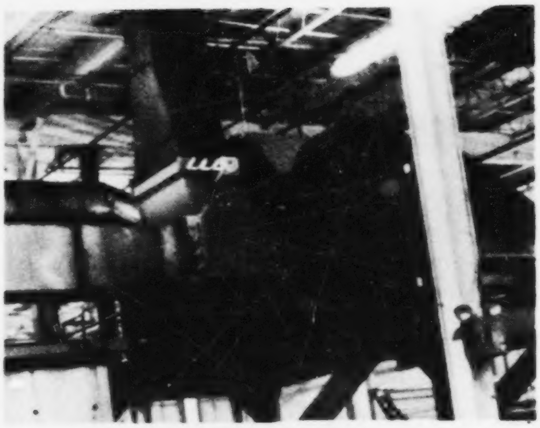


PHOTOGRAPH 1

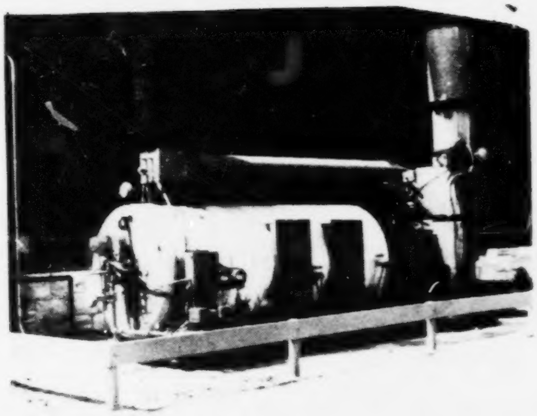
PHOTOGRAPH 2



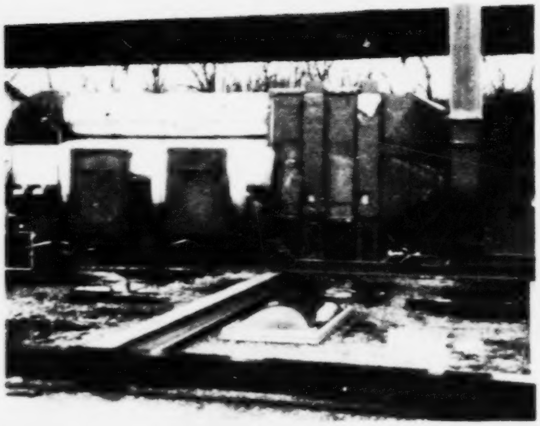
PHOTOGRAPH 3



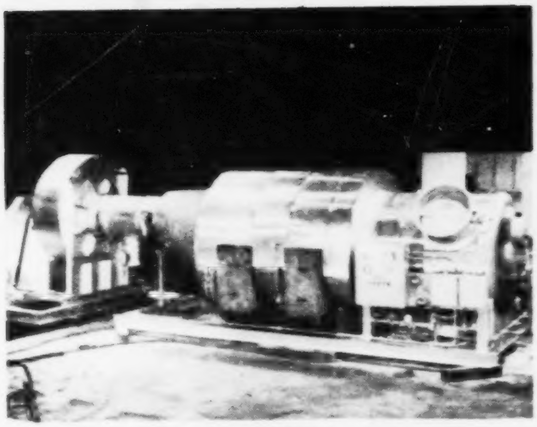
PHOTOGRAPH 4



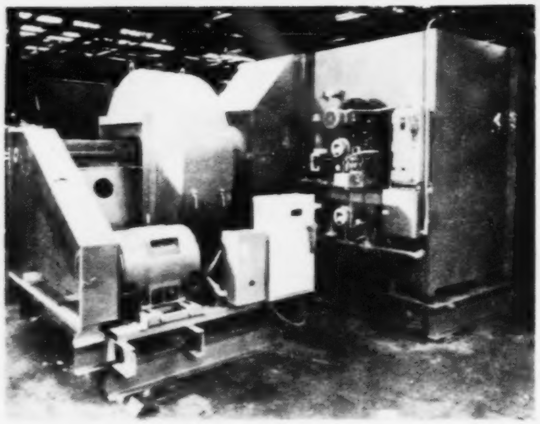
PHOTOGRAPH 5



PHOTOGRAPH 6



PHOTOGRAPH 7



PHOTOGRAPH 8

TABLE 1. RECOMMENDED CORRELATIONS FOR TRANSPORT PROPERTIES

Catalyst type	S/V (ft^{-1})	ϵ	L (ft)	X (π)	N_{Nu}, N_{Sh}, f
Torvex 2B (1/8 in. Hexcell Honeycomb)	268	0.61	0.0091	0.833	$N_{Nu} = 3.66\,(1 + 0.095\,N_{Re} N_{Pr} \frac{L}{X})^{0.45}$ $N_{Sh} = 3.66\,(1 + 0.095\,N_{Re} N_{Sc} \frac{L}{X})^{0.45}$ $f = 64/N_{Re}\,(1 + 0.0445\,N_{Re} \frac{L}{X})^{0.5}$
Thermocomb (8 c/in. Honeycomb)	695	0.6	0.00345	Normally 0.167–0.333	$N_{Nu} = 2.35\,(1 + 0.095\,N_{Re} N_{Pr} \frac{L}{X})^{0.45}$ $N_{Sh} = 2.35\,(1 + 0.095\,N_{Re} N_{Sc} \frac{L}{X})^{0.45}$ $f = 53.3/N_{Re}\,(1 + 0.0445\,N_{Re} \frac{L}{X})^{0.5}$
Oxycals	36.5	0.515	0.0133	–	$N_{Nu} = 0.51\,N_{Re}^{0.56} N_{Pr}^{0.333}$ $N_{Sh} = 0.51\,N_{Re}^{0.56} N_{Sc}^{0.333}$ $f = 0.5/N_{Re}^{0.15}$
Metal ribbon ("D" Series)	336	0.93	0.004	–	$N_{Nu} = 0.55\,N_{Re}^{0.5} N_{Pr}^{0.333}$ $N_{Sh} = 0.55\,N_{Re}^{0.5} N_{Sc}^{0.333}$ $f = (1-\epsilon)/\epsilon(5.2 + 3600\,(1-\epsilon)/N_{Re})$ $-\Delta P = \int_0^z G^2/2\epsilon^2\rho_g g_c f/L\,dZ + 2.1\,G^2/2\rho_g g_c$
Spherical catalyst pellets	$\frac{6\epsilon}{dp}$	Normally 0.35–0.4	dp	–	$N_{Nu} = 2.42\,N_{Re}^{1/3} N_{Pr}^{1/3} + 0.129\,N_{Re}^{0.8} P_r^{0.4} + 1.4\,N_{Re}^{0.2}$ $N_{Sh} = 2.42\,N_{Re}^{1/3} N_{Sc}^{1/2} + 0.129\,N_{Re}^{0.8} N_{Sc}^{0.4} + 0.4\,N_{Re}^{0.2}$ $f = (1-\epsilon)/\epsilon(3.5 + 300\,(1-\epsilon)/N_{Re})$

Note: Reproduced with permission from Shell Development Company

sylvania was having similar problems with visibility complaints from two tenter frames. A catalytic afterburner was installed on one frame and the before/after photographs are shown in Figure 8. The energy recovery is higher than in the first example because a recuperative heat exchanger is used as well as recycling of the hot, clean air. Operation since the first quarter of 1978 has been satisfactory (Photographs 1, 2, 3, and 4).

- An automotive assembly plant presently being constructed will have catalytic incineration in all of the paint curing ovens. They will be using waterbase paints, which are quite low in solvents but contain plasticizers, surfactants, and biocide. The purpose is to eliminate any visibility and odor problems and recover the energy value of the solvents in the vent gas. A large portion of the hot, clean air will be returned to the ovens to reduce fuel consumption. The smaller remaining portion is heat exchanged with ambient makeup air before exhausting to the atmosphere. Because the exhaust gases are free of the high molecular weight hydro-

TABLE 2. EFFECT OF SOLVENT LOAD ON FUEL CONSUMPTION

Basis:		
	10,000 SCFM Total Flow	Fuel Cost = \$2.25/mm Btu
	Toluene	Oven Temperature = 250° F
	ΔH = 17,613 Btu/lb = 4,196 Btu/SCF	Preheat required:
	No Heat Exchanger	Catalytic – 550° F, Thermal – 1,250° F

% LEL	ppm V/V	Meters Btu/h ΔH	Theoretical ΔT – ° F	mm Btu/h required to preheat	
				Catalytic	Thermal*
1	120	302.1	26.5	3.1	11.1
2	240	604.3	53.0	2.8	10.8
5	600	1,510.7	132.5	1.9	9.9
10	1,200	3,021.3	264.9	0.4	8.4
20	2,400	6,042.6	529.9	0	5.4
50	6,000	15,106.6	1,324.6	0	0

*Allows credit for heat released by combustion of solvent and no heat exchanger.

Note: In both catalytic and thermal incinerators, heat exchangers can be used to provide the preheat. Catalytic afterburners can run self-sustaining (zero fuel consumption) at any concentration above about 4 percent of the LEL.

TABLE 3.

BASIS: \$2.50/mm Btu
Preheat 250° F → 500° F operating temperature for catalyst
Preheat 250° F → 1,300° F operating temperature for thermal

$$\text{Fuel} = \text{SCFM} \times 1.085 \times (T_2 - 250) \Big/ \frac{2.50}{10^6} \Big/ 8{,}000\ \text{h}$$

$$= \text{Btu/h} \Big/ \frac{\$}{\text{mm Btu}} \Big/ \frac{\text{h}}{\text{yr}}$$

SCFM	Fuel-catalytic	Fuel-thermal	Annual \$ savings vs. thermal
2,000	13,020	45,570	32,650
10,000	65,100	227,850	162,750
20,000	130,200	455,700	325,500
50,000	325,500	1,139,250	813,750
100,000	651,000	2,278,500	1,627,500

Note: Annual fuel costs: 8,000 h/yr if no recirculation or recovery of heat.

TABLE 4.

BASIS: \$2.50/mm Btu
Preheat 250° F → 550° F operating temperature for catalyst
Preheat 250° F → 1,300° F operating temperature for thermal

$$\text{Fuel} = \text{SCFM} \times 1.085 \times (T_2 - 250)\ \frac{2.50}{10^6}\ 8{,}000\ \text{h}$$
$$= \text{Btu/h}\quad \frac{\$}{\text{mm Btu}}\quad \frac{\text{h}}{\text{yr}}\quad = \$/\text{yr}$$

SCFM	$/yr Fuel-catalytic	$/yr* Fuel-thermal	Annual $ savings vs. thermal
2,000	3,906	13,671	9,765
10,000	19,530	68,355	48,825
20,000	39,060	136,710	97,650
50,000	97,650	341,775	244,125
100,000	195,300	683,550	488,250

Notes: Annual fuel costs: 8,000 h/yr if 70 percent of heat exit incinerator is recovered in some form, e.g. recirculation, steam generation, air preheat.

Electrical costs for blower motor will average about \$467/yr per 1,000 ACFM; based on \$140/hp-yr and 300 ACFM/hp.

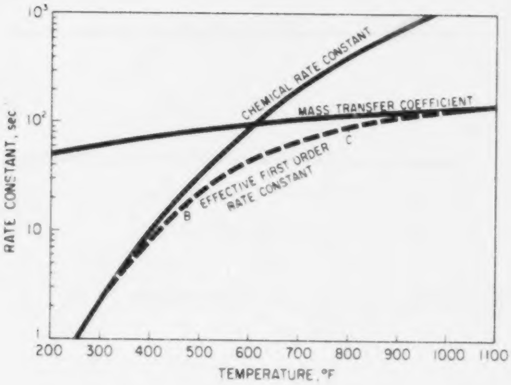


Figure 1. Effective first order rate constant and chemical and mass transfer rates contributing to it.

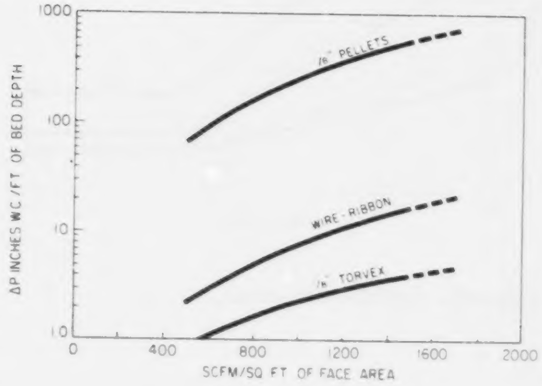


Figure 2. Pressure drop vs. flow.

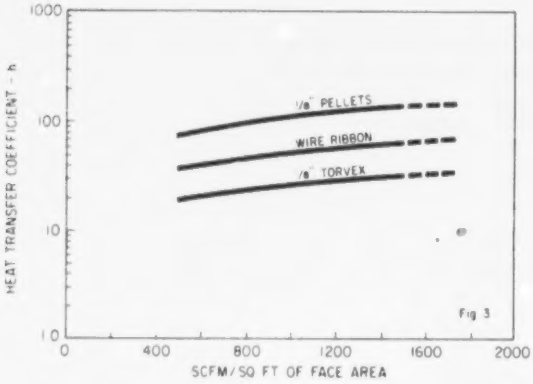


Figure 3. Heat transfer coefficient vs. flow.

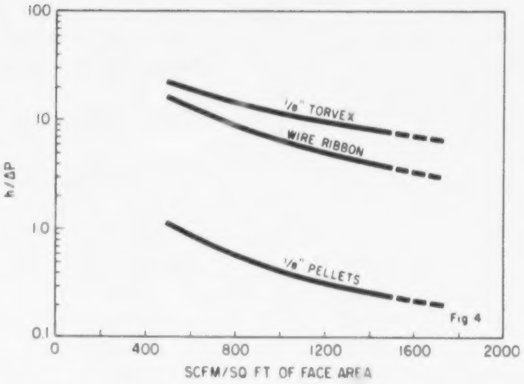


Figure 4. Ratio of heat transfer and mass transfer to pressure drop.

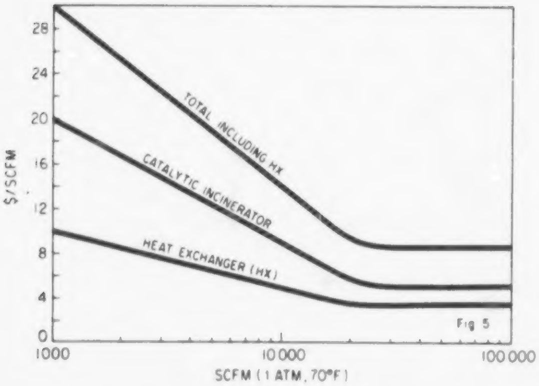


Figure 5. Equipment costs.

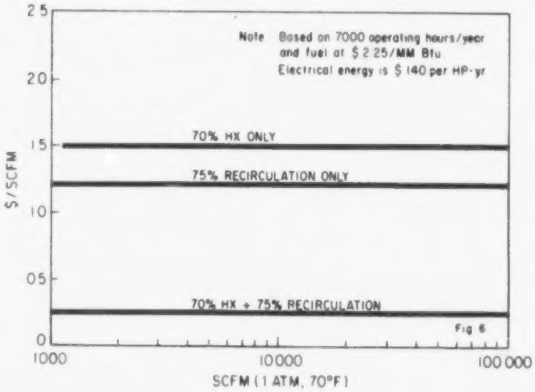


Figure 6. Annual operating costs.

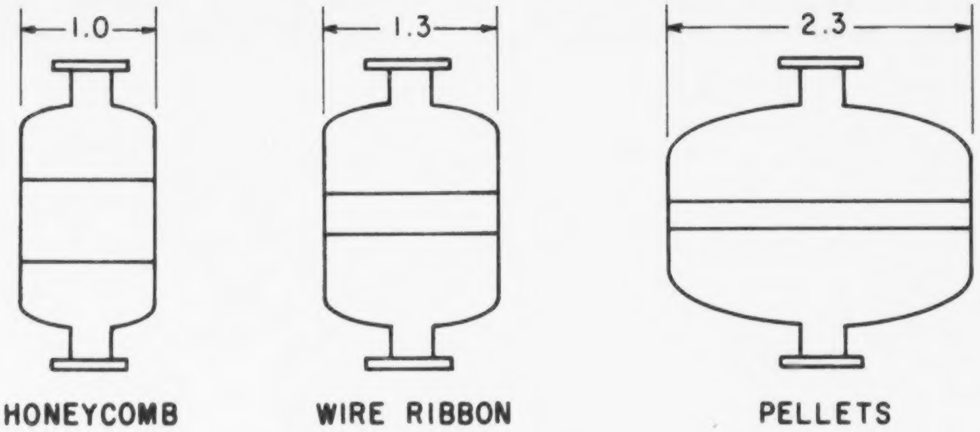


Figure 7. Vessel diameter vs. support type.

carbons the heat exchangers should remain at their design effectiveness and not require frequent cleaning.

- A 2-piece can plant in central New Jersey had an existing thermal incinerator designed to handle 12,000 SCFM and was using approximately $250,000/yr of fuel at 1977 prices. After retrofitting with a catalyst and reducing temperatures to 600° F, the plant engineer says, "the energy savings are very gratifying." The fuel bill for the first 9 months of operation is $100,000 less than during the 9 months when thermal incineration was used.
- An aluminum coil coater in northern New Jersey had a thermal incinerator but gas consumption exceeded his allocation, forcing him to use propane for fuel. The unit was retrofitted with a catalyst and the temperature reduced to 600° F. The fuel consumption dropped by more than 50 percent. As a result, the use of natural gas was resumed and the fuel cost reduced by more than 75 percent.
- A 2-piece can line in northern New Jersey utilized a thermal fume incinerator with a recuperative heat exchanger for approximately 1 year before retrofitting the unit with $21,000 worth of catalyst. Propane was the only fuel available to the plant. After approximately 6 months of catalytic operation, the plant manager reported his propane consumption had been reduced by 75 gal/h. Stack tests indicated more than 90 percent reduction of solvent hydrocarbon at a catalyst inlet temperature of 600° F. The catalyst cost was payed back in approximately 2 months.

REFERENCES

1. M. R. Miller and D. M. Sowards, "Solvent Fume Abatement by Ceramic Honeycomb Catalyst Systems," Franklin Institute First National Symposium on Heterogeneous Catalysis for Control of Air Pollution, November 22, 1968.
2. M. R. Miller and H. J. Wilhoyte, "A Study of Catalyst Support Systems for Fume Abatement of Hydrocarbon Solvents," *APCA Journal*, Vol. 17, No. 12, December 1967.
3. R. D. Hawthorn et al., "Afterburner Systems Study," Environmental Protection Agency Contract EHS-D-71-3, Shell Development Company, Emeryville, CA.
4. D. M. Sowards, Fixed-Bed Vapor/Solids Contacting Device, U.S. Patent 3,977,090, issued August 31, 1976.
5. H. L. Breckenridge and W. P. Jensen, "Survey of Energy Use in Metal Coil Coating," Contract EY-76-C-07-1570, U.S.

Dept. of Energy, EG&G Idaho, Inc., published February 1978.

6. "Catalyst Saves a Printer's New Market," *Textile World*, August 1976.

7. U.S. Environmental Protection Agency, "Control of Volatile Organic Emissions From Existing Stationary Sources," EPA-450/2-76-028, Vol. 1, November 1976.

RADIATION CURING FOR TEXTILE COATING

William K. Walsh, B. S. Gupta*

Abstract

This paper briefly outlines the technology of solvent-based fabric coating and the magnitude of the solvent emissions problem.

INTRODUCTION

The technological changes that occur in the fabric coating industry in the next 5 to 10 years will almost all be developments directed at reducing solvent emissions (ref. 1). The shape and nature of these developments will be determined to a large degree by the time frame imposed by government regulations (ref. 2). A short time frame will favor short-term solutions that will tend to become permanent, while a longer period should favor more technically complex answers. The technology of solvent-based fabric coating and the magnitude of the solvent emissions problem will be addressed further is this paper. Solvent-free, radiation curable coatings will be described and their potential for use in fabric coating will be compared to other possible technical solutions to the emissions problem that are being examined by the coatings industry. As is true with other industries with strong environmental concerns, the decisions made on these uncertain options will affect the fabric coating manufacturers' future for years to come. Regional and national economic well being will also be affected to some extent, as well as our trade balance, since imports from developing countries are already making significant penetration into this market.

Coated fabrics are textile materials covered with a film-forming substance. The fabric serves mainly to provide strength, and the film provides a functional purpose that the raw fabric is unable to perform. The variety of different textile materials, coating materials, and coating methods result in a large number of marketable products. The earliest coated fabrics were linen or jute impregnated with drying oil, leading to the name "oilcloth," which was first produced in volume in the 18th century. Nitrocellulose coatings appeared soon after, as did latex rubber, which produced synthetic leather and rainwear that was so satisfactory that it remained the standard for more than 50 years (ref. 3). Synthetic polymers were introduced in the 1930's and are used almost exclusively today. Acrylates and styrene-butadiene rubbers are presently consumed in large volume for back coating of upholstery fabrics and carpets. These are water-based latices and do not constitute a major emissions problem. The largest uses of vinyl coatings (plasticized polyvinyl chloride) are in automobile tops, upholstery, and low-cost apparel. These coatings, for the most part, do not require solvent evaporation.

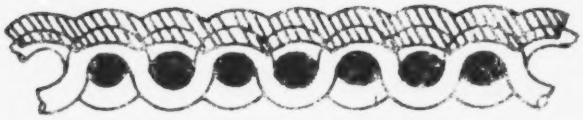
Polyurethane-coated fabrics are of the highest cost and best quality in the field, due to a number of desirable attributes which set them apart from other coatings (ref. 3). Such attributes are:

- warm, dry, pleasant handle,
- stability to washing and dry cleaning,
- high cold flexibility (without plasticizers),
- good wear properties and abrasion resistance,
- high breaking strength, elongation, and toughness,
- stability to oils and fats, and
- low density.

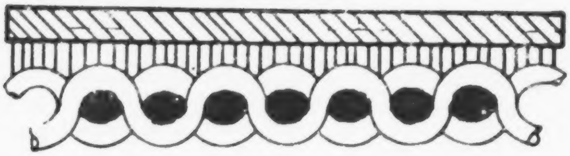
Urethane-coated textiles are finding applications in an increasing variety of apparel, domestic, and industrial goods. The annual consumption of fabric for coating exceeds 110 million square yards and for chemicals, over 20 million pounds, figures which are on an increasing trend. The two types of coating used are direct and transfer, illustrated in Figure 1. In the direct method, the coating collapses around the yarns, leaving a surface with the general appearance of the fabric. Substantial penetration of the coating into the fabric results in a

---

*School of Textiles, N.C. State University, Raleigh, NC.



DIRECT COATING



TRANSFER COATING

Figure 1. Direct and transfer coating.

stiffer end product, depending on the coating modulus. This type of coating is generally given to fabrics to stabilize them against yarn raveling and distortion (back coating), and to reduce penetration by wind and water (face coating). Some of the major end uses of the face-coated urethane fabrics are protective clothing, camping fabrics, military fabrics, and industrial fabrics.

In transfer coating, the penetration is highly minimized by either precuring the coating to some extent before applying it to the fabric, napping the fabric so that the coating adheres to the nap rather than to the yarns, or using a highly flexible tie coat such as foamed polyurethane. All of these methods lead to a fabric that is soft and flexible. This kind of coating is carried out in order to produce fabrics with leather-like appearance, soft hand, and durable properties. Applications include apparel, shoe uppers, handbags, luggage, upholstery, and numerous other domestic and industrial applications. The coating is usually cured in contact with a release paper, and the leather-like surface is formed using the pretextured release paper as a mold.

The excellent properties attainable with polyurethane coating are accompanied by two negative parts that have limited the extent of their use—high chemical cost and the solvent emission problem. These are not independent, since the cost of the solvents, which are evaporated, contributes to the high cost of the coatings. The urethane fabric coating section of the U.S. textile industry is the industry's largest air polluter, on a per pound (of fabric) basis, and is a major contributor on the basis of total emissions. The current production is about 65 million square yards of leather-like, transfer-coated (from release paper) fabrics for handbags, shoe uppers, and apparel; and about 50 million square yards of direct-coated (mostly rip-stop nylon) fabrics for camping and general outdoor use. The coatings on all these fabrics are applied at 15 to 40 percent in solvent, the great majority of which is released into the atmosphere. From these production figures, total emissions from the two processes can be estimated at around 10^7 lb/yr. A number of solvents are mixed in various proportions for different coatings, but toluene, dimethyl formamide, ethyl acetate, and methyl ethyl ketone comprise the bulk of the emissions.

Fabric coaters are quite concerned about this problem and are currently considering possible solutions. Incineration of stack gases is a partial solution, but is being used only minimally at present due to its high energy consumption. Recovery has not been deemed economical, mainly due to the mixed nature of the solvents ("randomly" mixed recovered solvents currently sell for only about 20¢/lb). The markets for coated fabrics are expanding and decisions on new equipment to meet this demand must soon be made. These forces, combined with increasing pressures to limit insults to the environment, make it imperative that exploration of alternatives not be delayed.

RADIATION CURING – A POSSIBLE ALTERNATIVE

Radiation curing involves coating with solutions of monomers and unsaturated, low molecular weight polymers (oligomers) and polymerizing, or curing the coating with radiation, either ultraviolet (UV) or electron beam (e.b.). No solvent is used and solution viscosity is adjusted by the ratio of monomer to oligomer.

Ultraviolet curing equipment uses medium pressure mercury lamps with intensities from 200 to 300 watts/inch (input energy). Usually several lamps in series provide curing speeds up to 1,000 ft/min. Electron beam equipment is either scanned beam, with electron energies over 250,000 volts, or the linear electrode type, with lower electron energies. All of these facilities require shielding and safety interlocks that add significantly to their cost. These increases are around $200,000 to $500,000 for e.b. and about $50,000 to $150,000 for UV. Excellent reviews and descriptions of the equipment and its characteristics have recently appeared (ref. 4). Ultraviolet curing gives excellent results for clear films and very thin (<0.2 mils) pigmented ones, and is generally believed to be less expensive in spite of its requirements for photoinitiator (1 to 5 percent on the coating weight). Electron beam is preferred for thicker, less transparent films and is mandatory for "buried" adhesives (e.g. under release paper).

These curing techniques present an attractive alternative due to (1) energy savings, (2) elimination of the cost of the solvent, and (3) elimination of air pollution. Further advantages are: higher line speeds, greatly reduced floor space, and better controls, due to a higher technological base.

ENERGY AND CHEMICAL COSTS

One of the most pressing societal problems that is likely to be mitigated by use of irradiation is the current shortage of all forms of energy. Since this shortage is projected to be a continuing problem, it is necessary that all segments of every industry study ways to reduce their requirements by more efficient utilization. The textile industry's main energy source is natural gas. As an example, a heat-setting operation given fabrics containing synthetic fibers or a curing operation to polymerize a fabric finishing resin requires the equivalent in natural gas of 3 to 4 million Btu/h at typical production rates, which amounts to about 1,000 kilowatts.

A typical radiation cure, by a rough comparison, would consume about 40 kilowatts at the same production rates when carried out by electrons and 200 kilowatts by UV. Thus, even for this simple operation, energy reductions of 80 to 90 percent are predicted. In present years, these considerations would not seem as important, but they may reach overshadowing proportions as our energy supply continues to decrease and needs continue to increase, a viewpoint which must be given serious thought when making decisions on process changes, updating, and future utilization of energy.

However, the picture doesn't appear as bright and compelling when actual cost figures are taken since the cost of other materials, such as the chemicals, completely overshadow the cost of the energy. This lack of clear and compelling economic advantage has essentially been the major reason for the slow development in the use of radiation techniques in textiles. Many producers have felt that unless a radiation cure could produce something that a thermal cure could not duplicate, there was little reason to consider a change. This picture has been somewhat mitigated by the coating industry's experience with particle board, can stock, and printing, which has demonstrated overall savings in terms of energy, floor space, and increased speeds. An example of the economics of high-speed e.b. coating is given in Table 1 (ref. 2).

Energy savings from switching to radiation are usually more than 90 percent with the added benefit of reduced dependency on natural

TABLE 1. ENERGY COST COMPARISON ELECTRON BEAM CURING VS. THERMAL CURING (ref. 5)

Operation criteria

Thermal curing	Electron beam curing
1. Coating application – white coating on aluminum foil	1. Coating application – white coating on aluminum foil
2. Solvent type coating – 35 percent solids	2. Coating type – 100 percent solids
3. Coating laydown – 6 lb/ream	3. Coating laydown – 2 lb/ream
4. Web width – 60 in.	4. Web width – 60 in.
5. Line speed – 500 FPM	5. Megarad dosage – 2 megarads (could be lower)
	6. Line speed – 500 FPM
	7. Processor voltage – 175 kV
	8. Processor output – 200 watts/in. = 12 kW
	9. Power input – 17.5 kW

Cost per hour

Thermal curing		Electron beam curing	
Heat: 6,000,000 Btu/h (natural gas) @ $2.50/mm Btu's	= $15.00	Power for curing: (electric)	
hp (fans) 50 hp = 38 kW @ $0.02 kWh	= 0.76	17.6 kWh @ 0.02	= $0.35
		Water – 1 Ton/h	
Chill water – 25 tons/h		300 GPH @ $0.20/m	= 0.06
6,600 GPH @ $0.20/m	= 1.32	Cooling @ $0.10/ton	= 0.10
Cooling @ $0.10 per ton	= 2.50		
Subtotal	= $19.58	Inerting gas – (using own generator)	
		Fuel: 244 SCFH natural gas @ $2.50/MCF	= 0.61
Exhaust treatment		Water: 1,920 GPH @ $0.20/m	= 0.38
Gas incineration or precipitation to meet EPA requirements. Costs normally 100 percent of processing heat costs	= $15.00	Power: 3.6 kW @ $0.02	= 0.07
		Total	$1.57
Total	= $34.58		

Energy savings/year – Assuming 2 shift or 4,000 h/year basis:
($34.58 – $1.57) × 4,000 = **$132,040**

gas availability. The cost of this energy per square yard of coated fabric varies from 0.5c to 2c and is comparable to the amortization cost for curing equipment, either thermal or radiation. It is essential, however, to avoid neglecting chemical costs, which are usually much higher. These costs overwhelmingly dominate the others and this fact makes it necessary that radiation curable resins either require less chemical add-on, be either cheaper or very close in price to the thermally curable resins, or offer a product or some other advantage great enough that the increased cost can be recovered in the marketplace through increased sales and/or unit prices. Fabric back coating, for example, currently uses acrylic latexes, at 45c to 55c/dry pound. Since radiation curable compositions that are being developed cost considerably more than this ($1.00 to $2.50/lb), it seems doubtful that they will be able to replace latexes (or vinyls) in any process where they are performing satisfactorily unless a clear product advantage can be shown, or until the narrowing of the chemical cost gap and the increase in energy prices reverse this imbalance. Thermally curable urethane coatings on the other hand, however, cost from $1.50 to $3.50/lb. Since many of the radiation curable compositions have a similar chemical basis, prospects seem quite good for the elimination of chemical costs as a factor and chemical savings are probable in some cases. Introductory prices for 100 percent solids, radiation curable, light-stable formulations suitable for fabric coating are being quoted in the range of $2.25/lb.

Film Properties

Lack of chemicals available that were suitable for high rates of polymerization has been another barrier in the utilization of radiation technology in the coatings of textiles. The research on textile radiation processes in the late sixties and early seventies relied almost completely on the versatile N-methylol acrylamide, which has a high polymerization rate constant, gives gel on polymerization, and has cellulose reactivity through the methylol group.

The current and rapid development of a number of fast curing compositions by suppliers to the coating industry has substantially changed this picture. Most of the systems designed for application in the particle board, can, and printing industries, however, generally give cured products that are too stiff for more than a limited number of textile applications. The reasons for the above compositions tending to be stiff can be found by examining the chemistry of radiation curing, excellent reviews of which are available (refs. 6,7). The basic equations (ref. 8) for the polymerization rate (R_p) and the chain length (D_p) in a chain growth, addition polymerization, illustrate some of the problems

$$R_p = \frac{k_p}{(k_t)^{1/2}} R_i^{1/2} [M] \qquad (1)$$

$$D_p = \frac{k_p}{(k_t)^{1/2}} R_i^{-1/2} [M] \qquad (2)$$

where k_p is the propagation rate constant for the growing chain, k_t is the termination rate constant for stopping the chain growth, R_i is the rate of initiation of growing chains, which is controlled by the radiation intensity, and M is the concentration of monomer. As R_i is increased (which must be done to achieve high line speeds), equation (2) shows that the D_p decreases. At the high radiation intensities necessary, the D_p of the polymers from most common monomers is so low that the material is useless as a binder or coating. This problem is solved by using monomers with high k_p (such as acrylates or vinyl pyrrolidone), monomers which form gel on polymerization (acrylates again) or, most commonly, monomers with two or more double bonds to give crosslinking and build up molecular weight. As polymer begins to form, k_t decreases due to the viscosity increase (diffusion of the growing chain ends is restricted) and rapid curing takes place. All of these techniques, however, lead to increased crosslinking in the cured film. As a result, most of the resin formulations that have been developed result in cured binder films that are much stiffer and less extensible than those normally used in pigment printing. To increase flexibility, reactive polymers (actually low molecular weight [1,000], multifunctional oligomers) are used. The double bonds are usually located on the ends of the molecule, and increasing the molecular weight moves the double bonds further apart, reducing the tightness of the network formed when the double bonds are polymerized.

Several approaches (refs. 6,9,10) have lead to compositions that, on curing, form elastomers with properties approaching those normally used in textiles. In particular, oligomers of flexible polyesters end-capped with diisocyanates and hydroxyethyl acrylate can be polymerized with monofunctional acrylates or vinyl compounds to give fairly soft, elastomeric films. The difunctional oligomer leads to crosslinking, the degree of which varies inversely with the oligomer molecular weight (or distance along the chain between the double bonds). It has been found, for example, that elongation at the break of the cured films varies inversely with the square root of the oligomer molecular weight. Inclusion of small amounts of low molecular weight multifunctional acrylic monomers lowers the elongation considerably (ref. 9). The film produced by these techniques has many of the characteristics of urethanes, since the urethane linkage is used in the oligomer backbone.

Using these approaches, several formulations have been developed that give cured film properties adequate for replacing solvent-based urethanes in fabric coatings. However, these are not sufficient. The fabric coating industry requires a wide variety of products with a convenient range of properties such as stiffness, elasticity, adhesion, water and solvent resistance, and flame retardancy. New application techniques must be explored to meet the extra demands of 100 percent solids coating. Preliminary work has been done in these areas (refs. 12,13,14,15) but much remains to be done.

OTHER ALTERNATIVES

Besides the approaches of solvent recovery or incineration, several other coating techniques are in the preliminary stages of development and could offer potentially viable solutions to the problem.

Water-Based Urethanes—

Aqueous dispersions of polyurethanes are now available and are being used by a few direct coaters for camping and outdoor fabrics. Techniques for transfer coating have not been developed for these materials. Their major drawback is their high energy consumption during drying and the accompanying bottleneck in drying speeds due to the higher latent heat of vaporization of the water.

Laminating With Extruded or Calendered Films—

Extrusion of polyurethane films or forming of the films by calendering of polymer chips is a common solvent-free technique in the vinyl coating industry. The equipment is very expensive and only suited for large production runs of similar materials and probably not for the multitude of special coatings manufactured by urethane fabric coaters.

100 Percent Solids, Thermoreactive Systems—

These are similar in principle to the radiation cured coatings in that polymerization takes place on the fabric. Generally two components are mixed before curing. Polymerization begins right after mixing, so it is generally done in-line immediately before the coating head, a process which is somewhat awkward and difficult to control.

High Solids, Thermoreactive Systems—

These are two component systems with some solvent added to control viscosity and minimize premature reaction. The technique is a compromise that would not eliminate solvent emissions, but may make the thermoreactive systems more practical (ref. 16).

Powder Coatings—

Powdered polymer is applied to the substrate in a spray and is melted and cooled to form the coating. This technique has been successful in some types of metal coating and is currently under investigation for transfer coating of fabrics (ref. 17).

SUMMARY

The use of radiation for curing of coatings and inks is still a relatively new technology, but it has become widely accepted in such areas as metal decorating, particle board filler coatings, package printing, and clear coatings on magazine covers and, more recently, on vinyl floor tile. The practice, briefly, involves substituting a polymerizable monomer for the solvent, and a low molecular weight reactive polymer (oligomer) for the polymer. The coating is cured by room temperature, in situ polymerization, instead of by solvent evaporation. The free-radical polymerization is induced by high intensity ultraviolet light (using an added photoinitiator), or less commonly, electron beam.

The technique has been, therefore, successfully introduced primarily in areas where traditionally coatings have been applied from solvent, because the advantages are the greatest. Elimination of pollution, energy savings, higher line speeds, and greatly reduced floor space are significant advantages, but eliminating the cost of the solvent is often the deciding factor.

Studies of the possibilities of transferring this technology into the field of fabric coating have been initiated in this laboratory and by others. These preliminary studies demonstrate the feasibility and potential economic attractiveness of the method and point out the remaining work to be done. This work involves development of the radiation-curable coating formulations that meet the needs of fabric coaters and demonstration by fabrication and testing of coated fabrics using these formulations.

All of the commercial radiation curing applications to date have involved coatings on relatively inflexible substrates. Fabric coating, on the other hand, requires soft, highly elastic films after curing—properties not heretofore obtainable by radiation curing due to the high degree of crosslinking in the films. A great deal of development in this area has already taken place, but still more is needed for producing at minimal cost, flexible films with a wide variety of properties suitable for the various types of fabric uses.

If radiation curing could be demonstrated as a technically and economically successful way of eliminating solvent emissions in urethane fabric coating operations, it is probable that it would be adopted by other processors of flexible substrates with similar pollution problems.

The other techniques described here are also deserving of study. It is possible that a combination of radiation and one or more of the other techniques would be the answer. It is clear that more time is needed to study these alternatives. There is much work to be done, however, and the effort must be begun in earnest.

REFERENCES

1. F. Schore, *Daily New Rews Record*, p. 13, March 6, 1978.
2. R. Dorchies, *Sources and Resources*, Vol. 11, No. 6, p. 25, 1978.
3. H.-J. Koch, "Dyeing/Printing/Finishing," *Inst. Textile Bulletin*, Vol. 1, p. 11, 1978.
4. First International Meeting of Radiation Processing, J. Silverman and A. R. Van Dyken eds., and *Radiation Phys. and Chem.*, Vols. 8 and 9, 1977, translation.
5. Data furnished by Energy Sciences, Inc., Bedford, MA.
6. S. H. Schroeter, "Annual Review," *Material Sci.*, Vol. 5, p. 115, 1975.
7. A. J. Vrancken, *Chem. Peintures*, Vol. 73, No. 1, p. 3, 1973.
8. A. Chapiro, "Radiation Chemistry of Polymeric Systems," *Interscience*, p. 132, New York, 1962.
9. W. Oraby and W. K. Walsh, "Coatings and Plastics Preprints," *J. Appl. Polymer Sci.*, Vol. 32, No. 2, p. 263, 1977, in press.
10. D. D. Howard and B. Martin, *Radiation Curing*, Vol. 4, No. 2, p. 18, 1977.
11. A. D. Fussa and S. V. Nablo, *J. Coated Fabrics*, Vol. 4, p. 170, 1975.
12. W. K. Walsh and B. S. Gupta, *J. Coated Fabrics*, Vol. 7, No. 4, p. 253, 1978.
13. W. K. Walsh and B. S. Gupta, *J. Coated Fabrics*, Vol. 8, No. 1, p. 30, 1978.
14. W. K. Walsh, and B. S. Gupta, *J. Coated Fabrics*, in press.
15. W. K. Walsh, et al., High Energy Radiation for Textiles: Assessment of a New Technology," Final Report to NSF, Grant GI 43105, October 1977.
16. C. Bluestein, *Sources and Resources*, Vol. 11, No. 6, p. 27, 1978.
17. C. Evans, *Sources and Resources*, Vol. 11, No. 26, 1978.

CONTROL OF AIRBORNE PARTICULATES IN TEXTILE PLANTS

Mansour H. Mohamed, Arthur C. Bullerwell*

Abstract

It is agreed that high concentrations of dust level in the working environment in textile plants represents a health hazard. There is a number of ways by which the dust concentration could be maintained below a certain level for every process. New machinery is designed with more emphasis on decreasing dust levels around them than was done in the past. With existing machines, engineering controls have been developed, which in most cases, are successful in meeting present Federal regulations.

Developments in processing machinery, in exhaust ventilation systems, and in filtration technology are reviewed from the standpoint of dust generation and removal.

INTRODUCTION

Knowledge of respiratory problems of textile workers has been traced back as early as 1713 in connection with flax and hemp mills (ref. 1). References to problems associated with cotton dust go back to 1863 (ref. 2). The respiratory disease resulting from the exposure to cotton dust, which occurs in a certain percentage of the work force, is called "byssinosis." Since cotton dust regulations are the most serious particulate control problems facing the textile industry at the present time, this paper will deal only with this subject.

From 1964 to 1971, a total dust concentration level of 1 mg/m^3 was established as the ceiling limit of exposure by the American Conference of Governmental Industrial Hygienists (ACGIH). A dust concentration level of 1 mg/m^3 became the Federal standard under the Occupational Safety and Health Acts of 1970 and 1972. In 1974, the National Institute for Occupational Safety and Health (NIOSH) recommended that the lint-free dust concentration be set at the lowest level feasible, but not to exceed 200 μg/m^3 of vertical elutriator cotton dust for all segments of the cotton industry.

METHODS OF REDUCING DUST LEVELS

Use of Cleaner Cotton

This means changes in harvesting and ginning practices, leading to a reduction in trash content of the cotton supplied to the textile industry. Almost all of the U.S. cotton crop is machine-harvested by two methods: machine-stripped cotton, which is harvested by stripping the entire cotton plant, and machine-picked cotton, which is harvested by spindle-type pickers. Machine-stripped cotton normally contains more trash than machine-picked cotton, although reports indicate that true comparisons are almost impossible and that levels did not correlate well with harvesting methods (refs. 4,5).

Ginning is performed to remove the seed from the cotton lint. This is the most logical step for trash removal. The amount of trash removed depends on the ginning conditions and the number of lint cleaners used. Ginners are always concerned with the quality of the lint cotton and fear damaging the cotton fibers by excessive cleaning. Although fiber damage was found to be greater with increased cleaning in ginning, no one investigated if increased cleaning could be balanced by a reduction in the number of cleaners in opening lines, which would reduce fiber damage in opening.

The amount of trash removed at the gin is controlled by the amount of seed cotton cleaning, the number of drying stages, and the amount of gin lint cleaning. Two stages of drying at 250° F decreased the dust level in a model card room by approximately 19 percent (ref. 4). Increasing the number of saw-type lint cleaners from zero to two was reported to cause a maximum decrease in dust levels in a model card room of 37 percent in one paper (ref. 4) and 52 percent (ref. 6) in another. Cocke and Hatcher (ref. 5) processed conventionally cleaned cotton through a Shirley Analyzer and

---

*School of Textiles, N.C. State University, Raleigh, NC.

Preceding page blank

obtained a 43 percent reduction in dust levels.

Blending Cotton With Manmade Fibers

Although this would not be suitable for every end-use application, it is a fact that the amount of cotton dust generated is directly proportional to the rate of cotton flow through the plant. Therefore, a plant using a 50/50 polyester/cotton blend, for example, will generate 50 percent less dust compared to a plant having to produce the same amount of 100 percent cotton yarn.

Washing

This is known to remove the majority of trash and dust in the cotton. This process is a common practice in producing cotton for medical applications. However, to produce yarns from washed cotton requires extensive research to eliminate the problem of neps and the increased friction due to the removal of the natural waxes that exist on the surface of cotton fibers.

Cotton has also been treated with steam (ref. 7). This process has been shown to decrease the irritant level in the model card room, but at present there are still questions about whether this is an effective means to decrease byssinosis throughout a cotton textile plant. The standard did not establish a higher allowable dust level for steamed cotton; however, mills processing washed cottons are exempted from the standard.

Use of Additives

It has been demonstrated (refs. 8,9) that the application of oils in the range of 0.4 to 1.5 percent reduced the dust level by up to 94 percent. This seems to be a very successful modification and is worthy of consideration. It is certain that the use of additives will require readjustments in further processes, but reports seem to indicate only minor problems.

Development of New Machinery

Old textile machinery was designed without serious consideration to the dust problems. As a matter of fact, some machines that were designed for the purpose of separating trash from cotton did not have any dust-collecting devices. Over the last decade or two, various machines were developed with much more emphasis on dust removal and collection. Examples of new machinery that help reduce dust exposure are automated opening lines, chute-feeding of cards, and open-end spinning. However, a large number of the machines in use today are of the old design, and the most effective method of controlling dust levels is the use of ventilation systems.

Use of Ventilation and Filtration Systems

Although there are general rules for the use of ventilation and filtration systems, various machines require different approaches to cover the major points of dust emission. Variations in building size and structure present problems. For example, in the case of looms the best ventilation will be achieved when the air vents are placed under the looms, which is not always possible. Every mill and every process has to be dealt with as a separate case.

Let carding be taken as a specific example, since the card is considered the greatest source of dust generation in a textile plant. There are many ways by which dust is captured from the major emission points. Suction plenums are added at the doffer, cylinder, lickerin, and other points. In other systems, orifices are added over the web takeoff area, the coiler, and the doffer. In many systems, a transparent cover is used over the web and lickerin areas. Although some design differences exist between systems, the control points are basically the same. With high-speed cards, undercard suction is necessary.

In most systems, the dust-laden air is passed through two stages of filtration: primary and secondary. The primary filter (sometimes referred to as the condenser) is a fine-mesh screen which removes the lint in the form of a mat that helps in filtering some of the dust. The waste is doffed into a hopper and is removed either manually or by means of a suction system to the waste room. The secondary filter is generally a rotating drum covered with a filter medium. Cleaning the dust off the filter is continuously done by means of stationary suction nozzles, and the dust is collected at a condenser. It is recommended that the clean air be returned to the plant air conditioning system, which acts as a third stage of filtration. Some of the air could be discharged to the outside and replaced by fresh air. The percentage of makeup air has a very important economical significance. In other systems, the third stage is an electrostatic precipitator followed by an air washer through which the air passes before it is returned to the plant atmosphere.

In other processes, the same control systems are used. The major differences between processes are the collection points and the rate and pattern of airflow. Variations in dust levels and size distribution between processes have been reported. The median particle size tends to decrease in going from carding to warping, and the particle size distribution tends to be skewed to the small end. The decrease in median particle size is probably due to the micronizing of trash by the cleaning operation. The median particle size was reported to increase in slashing and weaving areas. The chemical nature of the dust in slashing and weaving was found to be different, due to the chemicals added on the yarn during slashing. Based on these facts, the cotton dust standard treats the slashing and weaving areas differently from other textile operations, as mentioned earlier.

In drawing, dust control consists of collecting the air from the drafting roll cleaner system and filtering it rather than blowing the dust back into the room. The use of hoods over the creel area is advised. In combing, the collection of dust at the aspirator for further filtration, control of dust from the drafting zones and suction slot at the coiler are recommended. Hoods might also be installed over the combing area. In spinning, the broken ends collection system is used to collect dust, which is then removed in a central filtering system. In most of these operations, it is preferred to move the air downward through the machines.

Due to the large volumes of air handled, air velocities at the filters are normally high. Economically, it is advantageous to use high velocities. However, filtration efficiency is reduced and the pressure drop across the filter is increased with the increase in air velocity. This presents a definite need for research on the development of high-efficiency economical filters for fine cotton dust. The use of electrostatic precipitators for the control of fine cotton dust also requires further study. Washing the collecting plates might be turned into a water treatment problem.

An experimental wet-wall electroinertial air cleaner has been developed by the researchers at the USDA Southern Regional Research Center in New Orleans, Louisiana (ref. 10). Its design consists of a vertical tube equipped with coaxial charging wire and an air entrance tangential to the periphery of the tube so as to impart rotational flow. Dust entering the tube is charged by corona from the wire and is attracted to the tube wall by combination of the electrical centrifugal forces. A film of water flows down the inner wall of the tube, washing the dust down to a discharge sump. Dust removal efficiency of up to 99.0 percent with a 10.16-cm (4-in.) diameter, 1.22-m (4-ft) long unit operating at 5.66 m^3/min (200 ft^3/min) air flow rate was reported.

CONCLUSIONS

1. Cotton dust concentrations could be reduced by many ways, such as improving ginning conditions, use of additives, and blending with synthetic fibers.
2. Control technology using local and general ventilation systems with two or three stages of filtration seems to be the most successful method of lowering dust concentrations to levels near or below the levels required by the cotton dust standard. However, economic pressures on the textile industry will be increased due to the capital and running costs of such equipment. In addition, every plant and every process has to be dealt with on a case-by-case basis, which makes it necessary to custom design the air-cleaning equipment.
3. The textile machinery industry has placed more emphasis on dust cleaning in the design of new machinery. Thus, the severity of the dust problem in textile plants is expected to reduce considerably in the future.
4. There is still a need for the development of high-efficiency, economical filters to capture fine cotton dust at high air veloci-

ties without excessive pressure drop.

5. The use of additives and washing of cotton may require significant changes in processing and have yet to be proven economically feasible on a mill level.

REFERENCES

1. B. Ramazzini, "Diseases of Workers," *De Morbis Artificum of 1713,* W. C. Wright, translator, Hafner Publishing Co., New York, 1964.
2. National Institute for Occupational Safety and Health, "Occupational Exposure to Cotton Dust," NIOSH Report, U.S. Department of Health, Education, and Welfare, Washington, DC, 1974.
3. "Occupational Exposure to Cotton Dust," *Federal Register,* Vol. 43, Part III, June 23, 1978.
4. J. B. Cocke, R. A. Wesley, I. W. Kirt, and R. V. Baker, *Effects of Harvesting and Ginning Practices on Mill Dust Levels,* The Cotton Gin and Oil Mill Press, December 18, 1976.
5. J. B. Cocke and J. P. Hatcher, "Dust Levels in Experimental Card Room as Influenced by Cotton Variety and by Harvesting and Ginning Methods," Transaction of the ASAE, 1975.
6. S. P. Hersh, R. E. Fornes, and E. V. Caruolo, "Respirable Dust Levels Developed While Processing Cotton in a Model Card Room," *Cotton Dust,* Proceedings of ACGIH Symposium, Atlanta, GA, November 12-13, 1974.
7. C. Michaels and D. Whisnant, "Manufacturing Aspects of Steaming Raw Cotton To Minimize Toxic Effects Upon the Human Respiratory System," *Engineering Control of Cotton Dust,* proceedings of a conference at Clemson University, July 26, 1972.
8. J. B. Cocke, H. H. Perkins, and C. K. Bragg, "Use of Additives to Reduce Cotton Dust Levels," *America's Textiles R/B,* March 1977.
9. R. E. Fornes, R. D. Gilbert, and S. P. Hersh, "Collection and Characterization of Cotton Dust in a Model Card Room," Beltwide Production Research Conference, Atlanta, GA, January 10, 1977.
10. D. P. Thibodeaux, A. Banil Jr., and R. B. Reif, "A Wet-Wall Electroinertial Precipitator: A Highly Efficient Air Cleaner for Cotton Dust," IAS 76 Annual.

Session IV: SOLID WASTE POLLUTION CONTROL TECHNOLOGY

P. Aarne Vesilind, Session Chairman

TEXTILE SLUDGE CHARACTERIZATION

Robert G. Shaver,[*] Deborah K. Guinan[†]

Abstract

Analysis of sludge samples from six textile industry segments has shown that metals and organic wastewater pollutants concentrate in the solid phase of the sludge. The six industry segments sampled were wool scouring, wool fabric dyeing and finishing, woven fabric dyeing and finishing, knit fabric dyeing and finishing, carpet dyeing and finishing, and yarn and stock dyeing and finishing. Approximately 2,000 of the more than 5,000 textile operations in the United States fall into these segments.

The amount of sludge generated in 1974 on a dry/weight basis was approximately 38,430 metric tons. This accounts for about 12 percent of the total waste generated by the textile industry in 1974. Of the total sludge generated approximately 0.5 percent was determined to be heavy metals content with less than 0.1 percent chlorinated organic material. The heavy metals found included arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, and zinc. The concentrations of these heavy metals found in the various textile industry segments range from 3,600 ppm in yarn and stock dyeing and finishing to 21,000 ppm in wool fabric dyeing and finishing. The bulk of these metals are washed or rinsed from fabric into a mill's wastewater treatment system from such operations as scouring incoming greige goods, dyeing and printing cloth, yarn, and carpet, and applying various finishes. The chlorinated organics were not specifically identified, but such compounds as trichlorobenzene, polyvinyl chloride, perchloroethylene, and others are commonly used as solvents, dye carriers, and finishing agents. The total chlorinated organics found in the sludges analyzed range in value from 0.11 to 64.7 ppm.

INTRODUCTION

The information presented in this paper is the result of a study Versar performed for the U.S. Environmental Protection Agency under Contract No. 68-01-3178 to assess the industrial hazardous waste practices of the textiles industry. The program began in April 1975 and a final report was delivered in June 1976.

TEXTILE SLUDGE GENERATION

Processes

For the purposes of this study, the textiles industry was classified into the seven categories that had been used earlier in an EPA effluent guidelines study for this industry. It was agreed upon by the American Textiles Manufacturers Institute (ATMI), Versar, and EPA that the best method for categorizing the industry was by process, not product. These process categories and the Standard Industrial Classification (SIC) codes are given in Table 1. Six of these categories, excluding greige goods, have wet processes such as scouring, dyeing, printing, and finishing, which generate wastewaters that are treated onsite or sent to publicly owned treatment works. These treatment systems generate various amounts of sludge containing a variety of heavy metals and other chemicals related to textile processing.

Of the more than 5,000 textile plants in the United States, 2,007 were identified as performing wet operations and thereby generating wastewater. The remaining plants fall into Category C and perform only such dry operations as knitting and weaving. Greige goods facilities also have yarn preparation operations which include finishing yarn destined for knitting in an oil or wax emulsion and slashing warp yarns used in weaving with carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), or starch. But these operations generate no wastewater.

In the study, Versar visited a total of 80

---

[*] Versar, Inc.

[†] Association of American Railroads.

Preceding page blank

plants representing approximately 16 percent of the total production in the seven textiles industry segments. The major effort was focused in Categories D, Woven Fabric Dyeing and Finishing, and E, Knit Fabric Dyeing and Finishing, since over 69 percent of textile plants are engaged in either woven or knit dyeing and finishing. Wastewater treatment sludges from 14 selected plants were sampled and analyzed to determine, in some measure, the composition of this land-destined waste. Each plant was composite-sampled once per week for 4 weeks, taking samples from the clarifier underflow. The sludges were analyzed for heavy metals and chlorinated organics. The total number of samples analyzed was 112. Details on the sampling techniques, analytical methods, and pollutant parameters measured are presented in a later section of this report.

Location and Industry Breakdown by Process

Table 1 shows the distribution of textile plants by industry category. A breakdown of the number of plants performing dyeing and finishing operations by EPA region is given in Table 2. As shown in the breakdown in Table 2, 91 percent of the plants that potentially generate wastewater treatment sludges were located in EPA Regions I, II, III, and IV with 50 percent located in Region IV alone. Also, the textiles industry as a whole is heavily concentrated in the eastern part of the United States.

The 2,007 plants with wastewater loads are approximately 37 percent of the total number of textile operations in the United States. The remaining 63 percent are dry operations.

Because the industry was categorized on a process-oriented basis rather than by product, Table 3 shows the distribution of the plants by State and by process. Table 4 summarizes the process distribution.

Over 62 percent of the textile plants are engaged in greige goods manufacture. Of the remaining plants that perform dyeing and/or finishing operations, over 69 percent are in the woven fabric and knit fabric dyeing and finishing categories.

Amount of Sludge Generated

The amount of sludge generated in each of the six wet processing categories was determined for "typical" plants in each industry category. The characteristics of a typical plant are determined by industry survey in consultation with industry personnel. In all cases the sludges arose from wastewater treatment.

In looking at the sludge disposal problem, an interesting phenomenon was noted. Sludge disposal was found to be typically necessary in only two industry categories, Wool Scouring, and Woven Fabric Dyeing and Finishing. All plants visited in the Wool Scouring category found it necessary to dispose of sludge. About 40 percent of the plants (56 percent of the category production) engaged in Woven Fabric Dyeing and Finishing category found it necessary to dispose of excess sludge. Most facilities in the other industry categories generate sludge at a low enough rate to preclude the need to dispose of any excess. Therefore, a distinction was made between sludge requiring disposal (wasted) versus that left accumulating in treatment ponds (retained) (see Table 5).

Figure 1 summarizes the estimated State-by-State distribution of total wastewater treatment sludges. This illustration shows that 78 percent of sludges are generated in EPA Regions I, II, III, and IV.

It was estimated that 488 plants of the 2,007 identified, which perform wet operations, have wastewater treatment facilities (24 percent). ATMI estimates that these 488 plants comprise 65 percent of the total production of the 2,007 plants. The remaining 1,519 plants use municipal sewage treatment, which transfers the problem of sludge disposal and its associated costs to the municipalities. About 7 percent of the plants visited contributed 50 to 95 percent of the total wastewater load to the municipal sewage treatment system. Several of the municipal treatment facilities were constructed with plant funds and turned over to the municipality for operation and maintenance.

Ninety-six percent of the 488 plants with treatment systems are generating sludge in unlined aeration basins with potential for percolation to underlying strata. Four percent were found to have concrete lined aeration or settling basins. The lined ponds were found to be most prevalent in Category A, Wool Scouring, where 67 percent of the plants use them. Category E, Knit Fabric Dyeing and Finishing, was the only other industry category found to be using lined ponds to the extent of 12 percent of the plants in the category.

TEXTILE SLUDGE CHARACTERIZATION

Analysis of sludge samples from the six textile industry segments found metals and organic wastewater pollutants to be concentrated in the solid phase of the sludge. The heavy metals found include arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, and zinc. The bulk of these metals are washed or rinsed from fabric into a mill's wastewater treatment system from operations such as scouring incoming greige goods; dyeing and printing cloth, yarn, and carpet; and applying various finishes. Total chlorinated organics were determined but not further specifically identified.

Sampling Techniques and Analytical Methods

A representative number of dyeing and finishing mills in each category except C, Greige Goods, was sampled and the plants were chosen to be representative in terms of processing and fiber types used. Four-hour composite wastewater treatment sludge samples were collected from clarifier underflows returning to aeration ponds. Two separate sets of samples were taken, one for heavy metal and one for chlorinated organic analyses. Sampling was repeated at each plant once a week for 4 consecutive weeks.

Samples earmarked for heavy metal analysis were acidified with nitric acid to a pH of 2 for preservation. The samples for organics analysis were not acidified and were handled very carefully to avoid contamination. Total solids content was measured on unpreserved samples.

Sludge solids contents were below 2 percent and atomic absorption was appropriate for determining total trace metals. The samples for atomic absorption analysis were digested by heat and acid, the residue redissolved in acid, and sample volume adjusted with distilled water. The samples were then filtered to remove insoluble materials and aspirated directly into the flame source. The absorbance was recorded and the corresponding metal concentration determined.

Alternate methods were used to determine mercury and arsenic. Mercury concentration was measured by the flameless atomic absorption method using a quartz lamp as a radiation source to vaporize the mercury. Arsenic was determined either by atomic absorption or by the silver diethyldithiocarbamate method.

To verify that most of the heavy metals were associated with the solid phase, the sludge samples — nonacidified samples — were centrifuged and the solids dried and digested. Then the atomic absorption method, as mentioned above, was used.

The suspended solids measurement was made by filtering, drying, and weighing a known volume of sample.

Chlorinated organics were determined from the nonacidified sludge samples by gas chromatography. The samples were prepared by adjusting the pH to between 6.5 and 7.5, extracting with methylene chloride in hexane, concentrating the extract on an evaporating hot water bath, and injecting the extract into a gas chromatograph. The concentration of chlorinated organics was then calculated by integrating the output absorption trace.

Results of Sample Analysis

Heavy metals are generally found in municipal and industrial wastewater treatment sludges, however, we found no published data concerning the composition of textile plant wastewater treatment sludge. During this program selected samples were analyzed for metal content to determine the distribution of metals between the liquid and solid phases of the sludge. This was accomplished by comparing the results of atomic absorption analysis of digested samples of the entire sludge (solid and liquid phases) and of the suspended solids separated from the liquid phase in nonpreserved samples. Table 6 shows an example comparison of these metal concentrations and the metal concentration calculated from them for the liquid phase (dissolved). Most of the heavy metal content of the sludge is in the solid phase and not dissolved. The exceptions are lead, manganese, and zinc. Most of the lead and large parts of the manganese and zinc were apparently dissolved.

Chlorinated organics determinations for all samples were made on both the liquid and suspended solids phases. Table 7 compares the results from five woven fabric dyeing and finishing plants. Similar differentials between liquid and suspended solid phases of chlorinated hydrocarbon concentrations were found from other textile industry categories. Note that the concentrations in the liquid phase are all below the drinking water standard of 0.7 ppm for total organics. Like the heavy metals, most chlorinated hydrocarbons were found in the suspended solids phase.

Table 8 summarizes the results obtained on the five woven fabric dyeing and finishing plants sampled for all measured parameters. On a dry sludge basis, concentrations of various heavy metals and chlorinated organics are far above drinking water limits.

Table 9 summarizes the average total heavy metal and chlorinated organics found from all industry categories.

TREATMENT AND DISPOSAL PRACTICES

Treatment

A flowsheet of the prevalent wastewater treatment technology is shown in Figure 2. Plants in all textile industry categories were found to retain sludge in unlined aeration ponds, and Categories A and D were found to dispose of excess sludge in general purpose landfills, dumps, and/or landspreading on farm land. A few plants in Categories A and E were found to retain sludge in lined aeration ponds and one plant in Category E disposed of dewatered sludge in an approved landfill.

Disposal

There are various disposal and waste management practices being used for sludges by the textile industry. Discussions of five of these practices follow.

Lagoon Storage or Retention—
Wastewater treatment sludges are being stored and retained in the wastewater treatment systems, either in disposal ponds or in the bottom of ponds or lagoons that are used for aeration and activated sludge treatment. As this sludge builds up, it will eventually reach the level where other storage or disposal will be necessary.

Land Dumping—
Land dumping of wastewater sludges is practiced by some textile plants. Some instances of onsite dumping were found.

Land Spreading—
Wastewater treatment sludges have some fertilizer value and in some instances are being sprayed or spread on land for this value. Various techniques are used, often utilizing farm-type equipment or irrigation-type spray units.

General Purpose Landfills—
Some plants send their wasted sludge to general purpose landfills. These landfills are characterized by their acceptance of a wide variety of wastes, including garbage and other organic materials, and usually by the absence of special containment, monitoring, and leachate treatment provisions.

Only one instance was found where an approved landfill site was used for disposal of dewatered sludge. This was in EPA Region III.

Wet Oxidation of Sludge—
We found one plant that had installed a wet oxidation process (Zimpro Process) for treatment of wastewater sludge. This uses liquid phase oxidation of wastes at high temperatures and pressures and has the operational flexibility of achieving either partial or nearly complete oxidation, as needed. Wet oxidation can reduce the amount of sludge and make the remaining sludge easier to dewater. It also converts much of the nonbiodegradable organic material (measured as COD) to either oxidized innocuous components or biologically degradable material which can be recycled to the plant wastewater treatment system for destruction. This operation had not been in use since 1972 because the small amount of sludge generated in the wastewater treatment system made the equipment uneconomical to operate.

All plants with wastewater treatment systems retained some sludge in their treatment ponds. Disposal of sludge is necessary only when the solids level in the wastewater treatment system builds to a point where the efficiency of the biological system would be affected. In Table 10 is a summary of plants visited that dispose of sludge. Local offsite disposal of sludge is usually within 16 km (10 miles) of the plant. Some of the plants that used onsite disposal of wasted sludge preferred to dispose of the sludges offsite in sanitary landfills and were seeking permission from local authorities to do so.

CURRENT REGULATORY STATUS

Wastewater treatment sludges from several textile industry categories:

SIC 2231 - Wool Fabric Dyeing and Finishing,
SIC 2261 - Woven Fabric Dyeing and Finishing,
SIC 2250 - Knit Fabric Dyeing and Finishing,
SIC 2269 - Yarn and Stock Dyeing and Finishing,
SIC 2279 - Carpet Dyeing and Finishing, and
SIC 2299 - Wool Scouring

have been incorporated by EPA into the September 12, 1978, draft of regulations under Section 3001 of RCRA (PL 94-580), which deals with criteria and listing of hazardous wastes. This draft is currently being circulated within the agency and to interested parties for comments.

DEWATERING OF WASTE ACTIVATED SLUDGE

Eugene J. Donovan, Jr.*

Abstract

Sludge dewatering is often an integral step in the ultimate disposal of solids removed from wastewater treatment systems. Waste activated sludge from biological treatment contains 95 to 98 percent moisture and is relatively difficult to dewater. There are a number of alternative dewatering processes available, each of which may have several variations. Processes may include land spreading for solar evaporation, sand bed drying with or without chemicals, and various mechanical systems which usually incorporate chemical addition. These include vacuum filters, centrifuges, pressure filters, and the relatively new belt filter press devices.

The selection of an appropriate and cost-effective dewatering system involves the evaluation of the process performance on the specific sludge, consideration of the ultimate disposal selected for the sludge, and various site specific factors. This paper reviews the application of the various sludge dewatering processes to waste activated sludges and outlines a step-wise approach to the evaluation and comparison of alternatives. Typical results and costs for dewatering waste activated sludge are presented herein.

INTRODUCTION

Dewatering of waste activated sludge is an element in the handling and ultimate disposal of the excess sludge produced by biological treatment of textile plant wastewater effluents. Dewatering processes remove water from a sludge to the extent that its physical form is changed essentially from that of a fluid to that of a damp solid. Major dewatering methods include vacuum filters, centrifuges, pressure filters, belt filter presses, sand-drying beds, lagoons, and land spreading. The decision to incorporate a dewatering step into a sludge handling scheme is based on the requirements of the ultimate sludge disposal option selected, which is usually site specific. Conversely, the ultimate disposal method selected is a factor in the evaluation and selection of an appropriate sludge dewatering process. Figure 1 shows the relationship of dewatering alternatives in various sludge handling schemes. The application of the various sludge dewatering processes to waste activated sludges is reviewed, and an approach to the evaluation and comparison of alternatives is presented, including data on performance, sizing, and costs of the alternatives.

WASTE ACTIVATED SLUDGE CHARACTERISTICS

Excess activated sludge is generated by the conversion of a fraction of the organic matter in wastewater to biological cells. The quantity of excess sludge depends on the biological system design (flood to microorganism ratio), raw waste characteristics, and effluent solids. For textile wastes, the solids production generally ranges from 20 to 50 percent of the BOD removed, plus the influent solids incorporated into the sludge, less effluent solids. Typical extended aeration systems utilized in the textile industry produce a relatively stable waste activated sludge, whereas sludge from high-rate systems may require further stabilization, through digestion, prior to dewatering or disposal.

Waste activated sludge from secondary clarifiers is a liquid containing 98 to 99.5 percent water. Gravity or dissolved air flotation may be incorporated into sludge-handling systems prior to dewatering or disposal.

The water contained in the sludge is distributed into three general classifications, free or between-cell water, bound or capillary water, and intercellular water. Free water can largely be removed by thickening or by drainage. Dewatering devices are utilized to increase the rate and amount of free water removal, and to

---

*Senior Engineer, Hydroscience, Inc., Westwood, N.J.

Preceding page blank

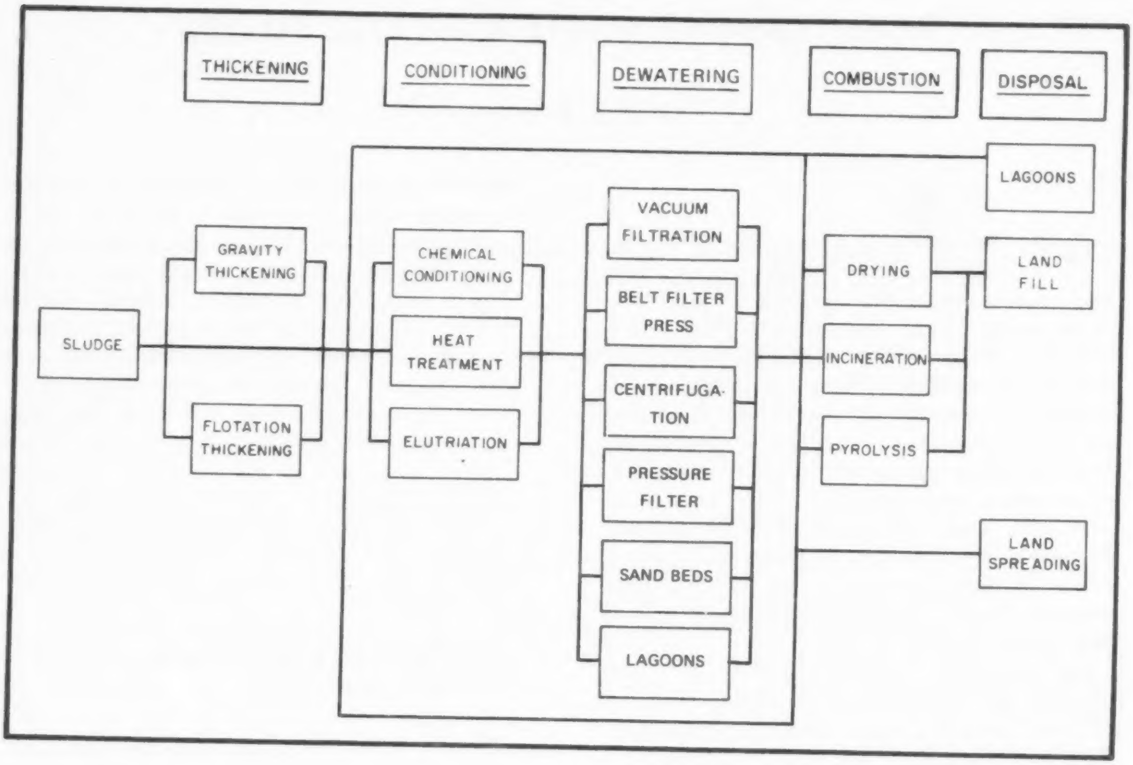

THICKENING
CONDITIONING
DEWATERING
COMBUSTION
DISPOSAL
SLUDGE
GRAVITY THICKENING
FLOTATION THICKENING
CHEMICAL CONDITIONING
HEAT TREATMENT
ELUTRIATION
VACUUM FILTRATION
BELT FILTER PRESS
CENTRIFUGATION
PRESSURE FILTER
SAND BEDS
LAGOONS
DRYING
INCINERATION
PYROLYSIS
LAGOONS
LAND FILL
LAND SPREADING

Figure 1. Schematic diagram of sludge handling alternatives.

form a cake. Various organic and inorganic chemicals are utilized to neutralize the bonding forces by coagulating sludge particles and freeing the bound water for subsequent removal by dewatering devices. Intercellular water, which requires rupture of the cell wall to free the water, is not removed to any great degree by dewatering systems.

Removal of free water from activated sludge produces a sludge of 4 to 6 percent solids, while removal of the bound water by chemical conditioning and dewatering results in sludge cakes containing from 12 to 25 percent solids. Further reduction in the moisture content involves evaporation and heat drying.

MECHANICAL DEWATERING ALTERNATIVES

Figure 2 is a schematic diagram of the major elements of the plate and frame pressure filter and of the rotary drum vacuum filter dewatering systems. These systems generally require substantial quantities of chemicals, typically ferric chloride coagulant and lime, for dewatering of waste activated sludges. Polymers have been utilized in place of the coagulants, and other materials such as pulverized ash or cement dust have been used for body feed. A precoat may be applied to the filter media prior to sludge dewatering to prevent blinding, to increase solids capture, and to allow easier cake discharge. In the case of the filter press, the precoat would be applied in a thin cover on the filter media prior to each filtration cycle, while for a precoat vacuum filter, the precoat would be applied as a relatively thick layer which would be gradually shaved off along with deposited sludge cake as the rotating drum moved past a discharge knife.

The filter press is operated on a batch basis. Each cycle consists of load, pressure, drain, and cake discharge steps, and ranges from 2 to

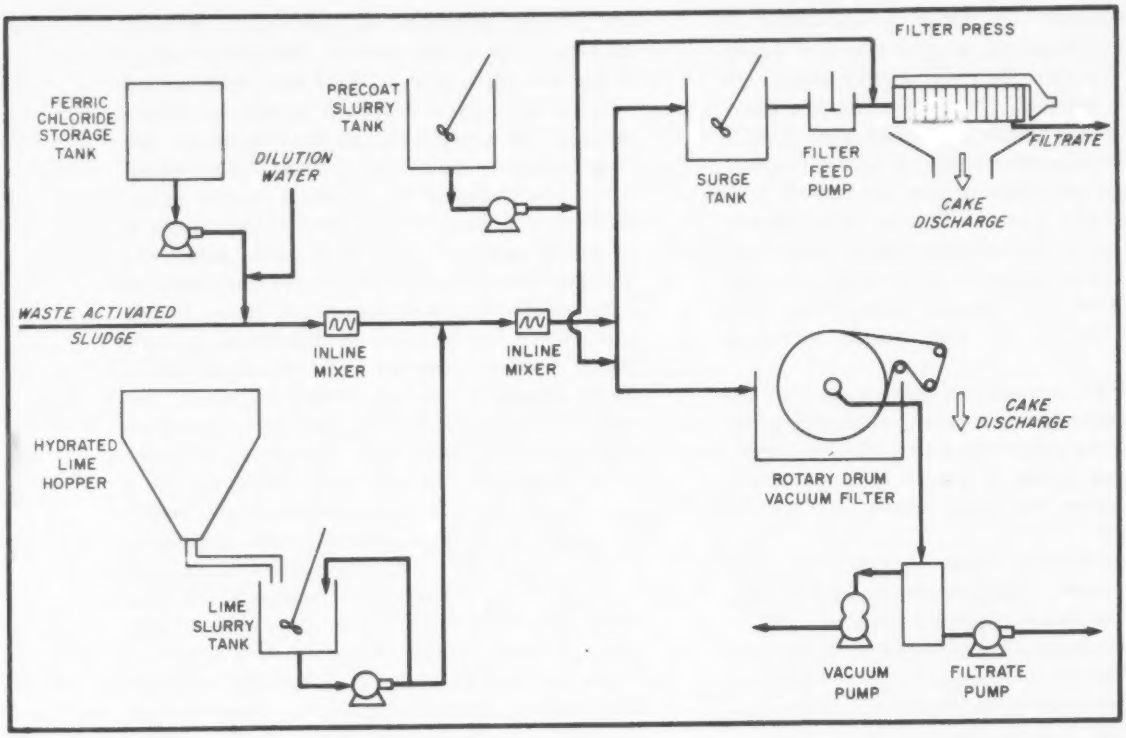

FILTER PRESS
FERRIC CHLORIDE STORAGE TANK
PRECOAT SLURRY TANK
DILUTION WATER
SURGE TANK
FILTER FEED PUMP
FILTRATE
CAKE DISCHARGE
WASTE ACTIVATED SLUDGE
INLINE MIXER
INLINE MIXER
CAKE DISCHARGE
HYDRATED LIME HOPPER
ROTARY DRUM VACUUM FILTER
LIME SLURRY TANK
VACUUM PUMP
FILTRATE PUMP

Figure 2. Flow diagram — vacuum filter and pressure filter.

4 hours. The rotating vacuum filter operates continuously. Sludge is picked up on the revolving drum from the vat, passes through a drying zone, and is discharged from the media.

The pressure applied to the sludge in the pressure filter by the feed pump is limited by practical design considerations. However, since increased pressure can reduce cycle time and increase cake solids, pressures of about 7 atm for activated sludge dewatering have been found to be satisfactory. The vacuum filter utilizes a vacuum to draw water from the sludge and is therefore limited by the vacuum which can be applied, usually in the range of 35 to 60 cm of mercury.

Historically, the vacuum filter has been widely used for dewatering wastewater treatment sludges. The use of the pressure filter, however, has received more attention in the last several years due to potential economic advantages in situations where drier and less sludge cake is advantageous for subsequent sludge processing, such as incineration or long hauls to limited landfill sites.

Bench-scale testing is conducted to determine chemical requirements. Optimum chemical dosages can be determined by the Buchner funnel test or the capillary suction timer test, in which sludge is dosed with varying amounts of chemicals and the relative ease with which free water can be removed is measured.

Small cells or pilot units are available to determine the need for precoat, the volume of sludge after dewatering, and cycle time required to size the pressure filter. A standard leaf test in which a vacuum is applied on 93 cm^2 (0.1 ft^2) of filter media in a sludge sample for various time periods can provide information required for media selection and sizing a vacuum filter. Appropriate scaleup factors are applied to leaf test data when used for sizing full-scale systems. Pilot scale testing to optimize design parameters and to obtain variability data on a sludge may, at times, be advisable, particularly for large installations, or where comparisons of specific types of equipment or various dewatering systems are desired. In general, for smaller sludge quantities or in cases where only small quantities of sludge from pilot treatability studies are available, design parameters are developed from bench tests and from experience with similar sludges. Figure 3 presents typical pilot test data on dewatering activated sludges with the pressure filter and vacuum filter. Final cake solids are based on total solids including chemicals.

Figure 4 is a schematic diagram showing the major elements for dewatering sludges by centrifuge and the relatively new belt filter press. Both systems utilize polymers to agglomerate sludge particles into large masses and to free bound water.

There are various types of centrifuges, but the solid bowl countercurrent centrifuge, which is in effect a high-rate settling unit, is the type most commonly selected for sludge dewatering. This type of centrifuge consists of a bowl and conveyor that rotate at slightly different speeds. A conical section in the bowl at one end forms the dewatering beach on which the conveyor screw pushes sludge solids to outlet ports. The centrate discharges over a weir that controls the depth of sludge in the centrifuge. Polymer is usually injected into the inlet line to the centrifuge. Major variables that affect the performance of the centrifuge include the pond depth, rotation speed, differential scroll speed, feed rate, and sludge conditioning. Full-scale designs should be based on scaleup from pilot tests, where possible, since bench tests do not provide the needed data on throughput and cake solids performance.

The belt filter press has been quite extensively used abroad and is rapidly growing in popularity in the United States. In Europe there are over 1,000 installations, while in the United States there are predictions that up to 400 or more units will be installed in 1978-79. There are some 8 to 10 manufacturers of various types of belt filter devices, each of which has different patented features and configurations. Typically, a belt press will consist of three distinct operations. The first is a simple gravity drain section in which the bound water freed by chemical addition is removed. The second operation involves the gradual pressing of the sludge between two converging parallel moving belts under tension. The third section is a shear zone, where the sludge between the two belts is passed over a series of rollers, causing the formed sludge cake to shear, further releasing more bound water. Some equipment incorporates an optional fourth stage, which exerts higher pressures on the sludge to maximize water removal. On activated sludges, however, this stage only increases the cake solids by a few percent at most. Bench-scale tests can be used to determine approximate polymer dosage requirements, and a hand squeeze test of sludge between two pieces of the press belts can provide an approximation of the cake solids. The sizing of equipment depends to an extent on the dewatering rate in the gravity drain section. Laboratory-scale belt press tests are conducted to develop design sizing. There are no general standards for measuring the actual throughput of sludge. Manufacturers have been developing data through pilot testing, however, the measurement of actual throughput and performance of a machine is best determined by pilot testing. Various manufacturers have mobile units, which can be used to develop a design sizing.

Figure 5 presents results of several pilot dewatering tests using the centrifuge and belt filter press. The lower polymer requirements and higher cake solids generally achieved by the belt filter press compared to the centrifuge can be noted. Generally, it was found that dosages above the minimum polymer dosage required to agglomerate the sludge particles resulted in a slight increase in cake solids. The range of results with different belt press machines and different sludges indicate the desirability of pilot tests for final system scaleup and sizing.

LAND DEWATERING OF SLUDGES

Dewatering of sludges on land includes the use of open or closed sand-drying beds, lagooning, and application to the land. Sludge that is dewatered by a land method should be relatively stable to achieve satisfactory results and to minimize odors. For leachate and runoff drainage from land disposal sites, consideration of potential effect on surface and groundwaters is required. The necessity for under drainage, normal for sand-drying beds but optional with

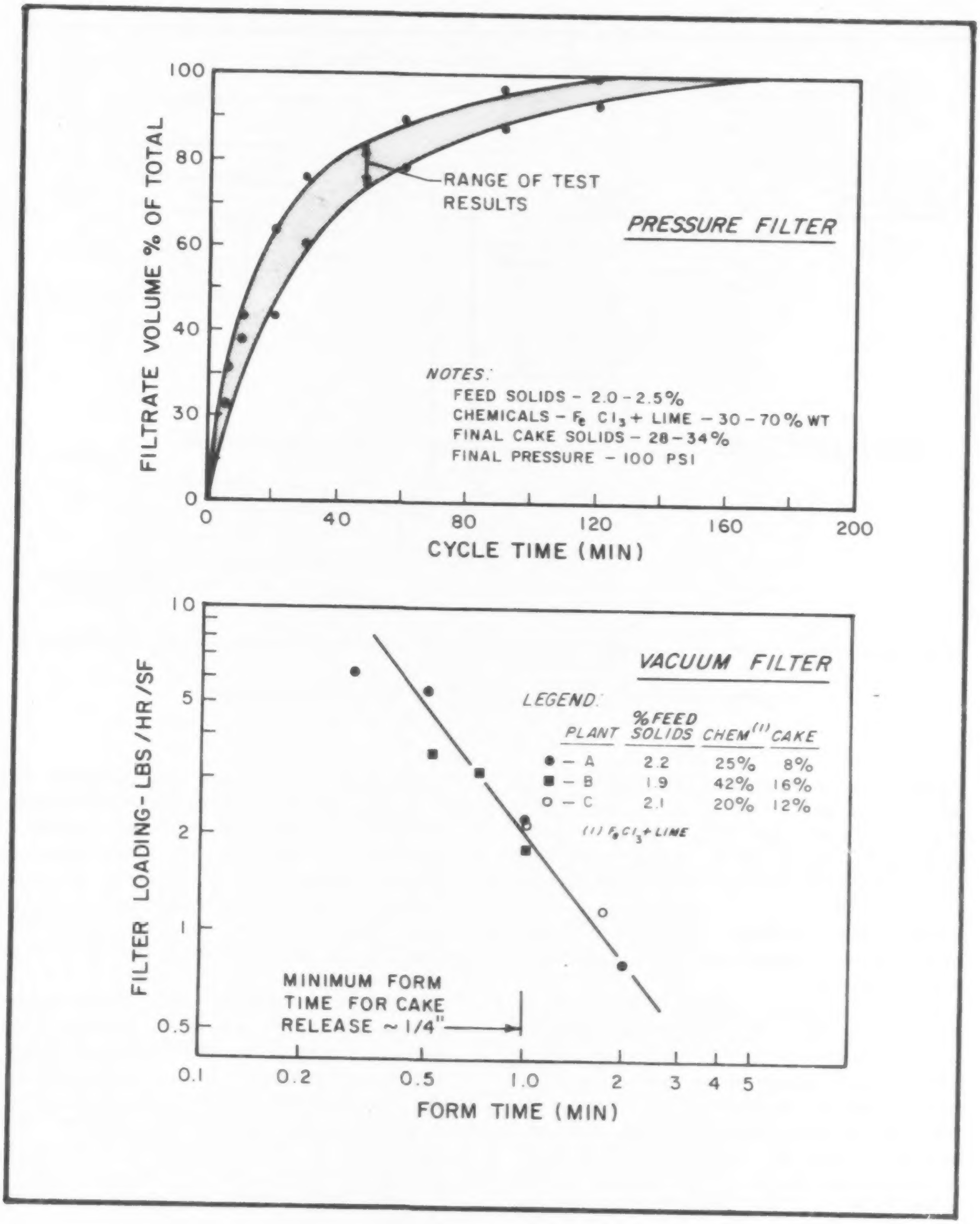


Figure 3. Vacuum filter and pressure filter WAS dewatering test results.

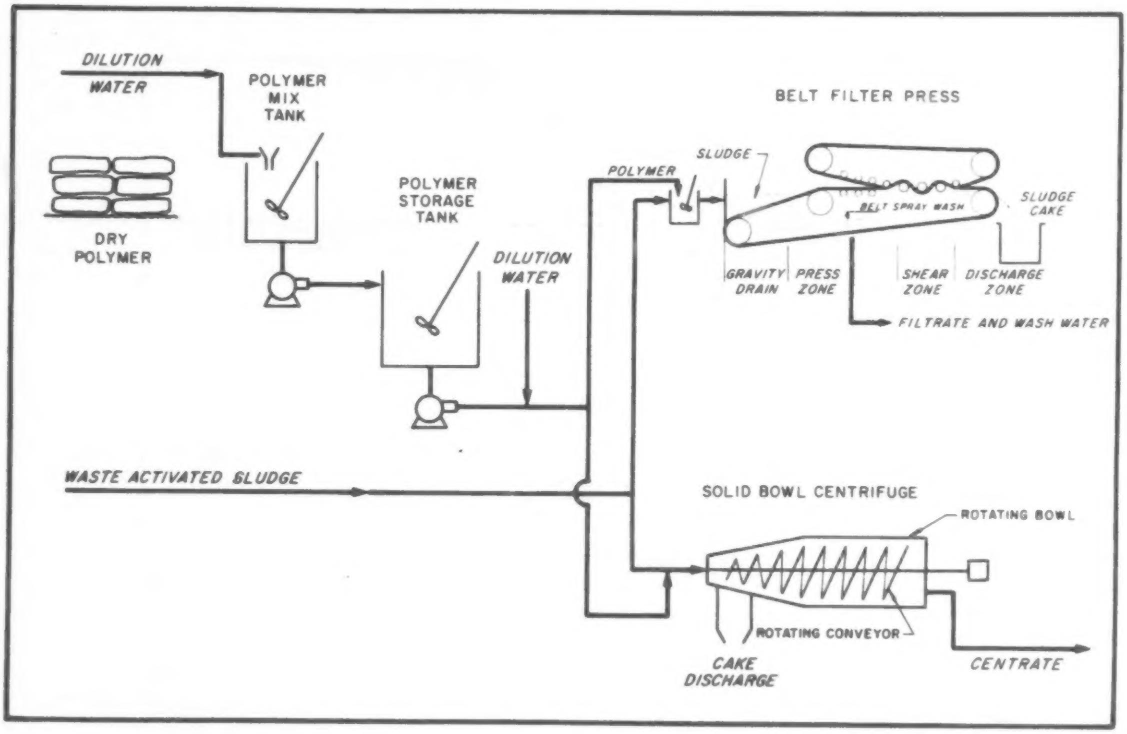

DILUTION
WATER
POLYMER
MIX
TANK
DRY
POLYMER
POLYMER
STORAGE
TANK
DILUTION
WATER
BELT FILTER PRESS
POLYMER
SLUDGE
SLUDGE
CAKE
BELT SPRAY WASH
GRAVITY
DRAIN
PRESS
ZONE
SHEAR
ZONE
DISCHARGE
ZONE
FILTRATE AND WASH WATER
WASTE ACTIVATED SLUDGE
SOLID BOWL CENTRIFUGE
ROTATING BOWL
ROTATING CONVEYOR
CAKE
DISCHARGE
CENTRATE

Figure 4. Flow diagram – belt filter press and centrifuge.

lagooning and land applications, requires evaluation. Many parameters affect the design and selection of a land dewatering system. A principal mechanism is drying through evaporation; therefore local climatic conditions such as amount and rate of precipitation, air temperatures, humidity, wind velocity, and percentage of sunshine are particularly relevant to a design.

Sand bed designs generally consist of enclosed beds with an underdrain system, overlaid with several layers of gravel and a layer of sand. Sludge is applied to the sand layer at depths consistent with design conditions for the drying time and sludge cake consistency desired. The design of the beds is influenced by the length of time required for the sludge to dewater to a consistency at which it can be removed from the bed and hauled to final disposal. Use of covered beds will greatly reduce the time required for dewatering, and conditioning chemicals such as polymers will also accelerate dewatering. Drying periods range from 1 to 2 weeks with chemicals, and from 2 to 6 weeks or more without chemicals, depending on weather conditions. Sizing of sand beds is based on local experience and general design factors. Testing on test sand beds can be conducted to obtain data on drying time, cake consistency, and underdrain quality, and factored with weather conditions to develop design sizing.

A sludge drying lagoon is a low-cost, simple system for sludge dewatering that has been commonly used in the United States. Sludge lagoons are generally not recommended since they are particularly susceptible to odors and nuisance conditions. They can stabilize and consolidate sludge with very little attention though, if properly sized and operated. Typically sludge is deposited in a lagoon at depths of 2 to 4 feet. Water drains into the soil or is evaporated. Under drains may be used where drainage to groundwater is not acceptable, or where permeable soils are not available. Two lagoons are usually provided, one being filled, one be-

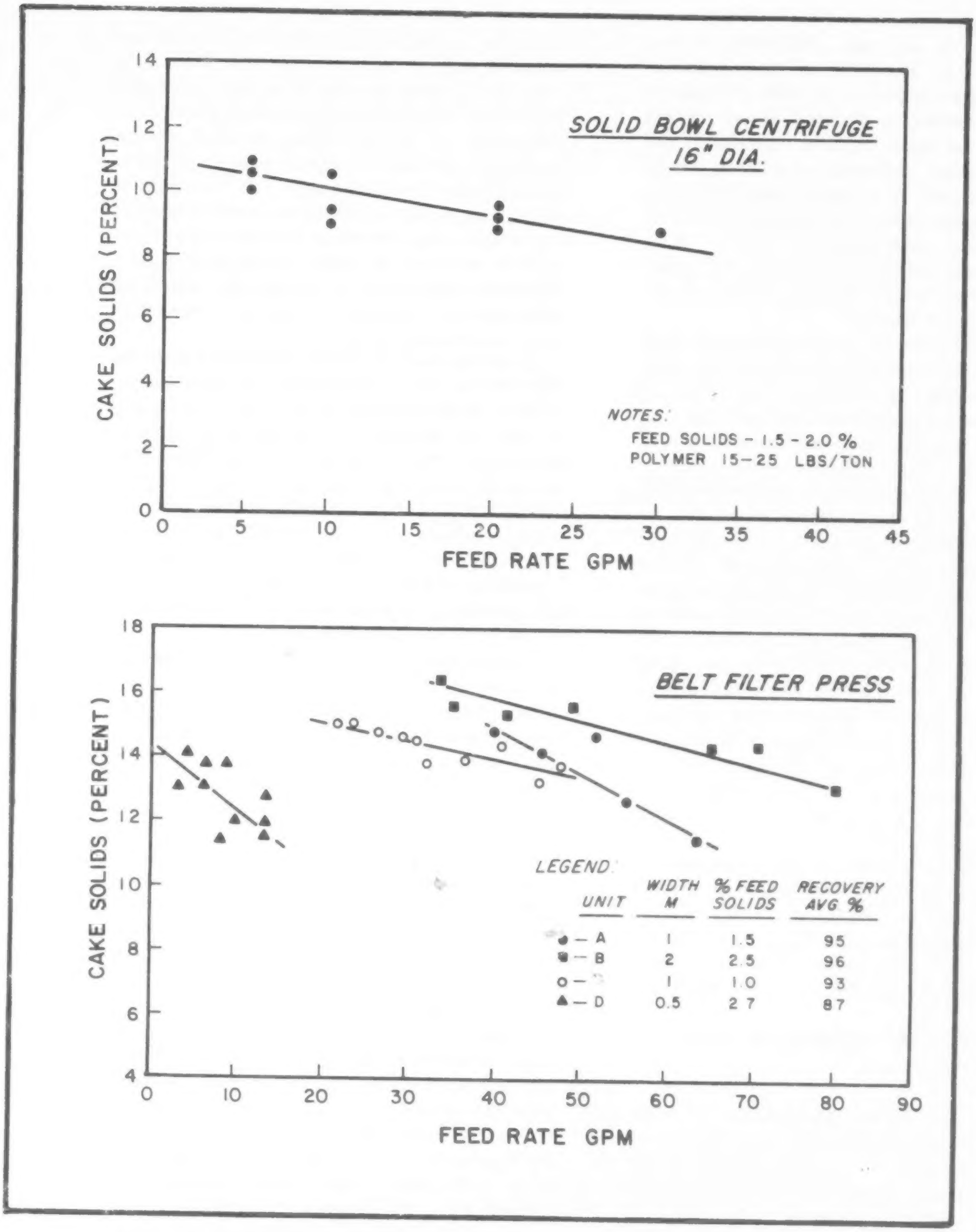


Figure 5. Belt filter press and centrifuge WAS pilot plant dewatering test results.

ing allowed to dry out. Following drying periods of 3 to 5 months or more, the dewatered sludge is removed with a front-end loader and hauled to disposal. Sizing drying lagoons can be based on local experience and small-scale tests, factoring in climatic conditions. Where land is available, relatively conservative design factors can be used in the absence of local experience or testing. Area should be reserved for expansion of the lagoon system in the future, should actual results necessitate more volume.

Sludge spreading on land is receiving some attention in the last few years and has been done at a number of locations. The effects of various factors and the development of loading parameters are in the developmental stage. Groundwater contamination and the effect of the sludge constituents on a crop grown on the land are factors to be evaluated in a specific application. Where land can be dedicated to sludge disposal only, high rates of sludge spreading may be feasible. The sludge is incorporated into the soil and there is limited to no vegetation. Rainfall runoff and leachate must be adequately considered in a design of a land application system. Discing deposited sludge can prevent surface blinding and minimize odors; the need for and advantages of this procedure should be evaluated. Sizing of land application systems depends upon a variety of considerations, including sludge nutrients, salt and heavy metal content, type crop, if any, to be grown and harvested, soil type, land characteristics, groundwater, and aesthetics. Each site requires an evaluation of the various factors. Where feasible, particularly for large installations, test plots should be operated and monitored for at least 6 months to a year.

EVALUATION AND COMPARISON OF ALTERNATIVES

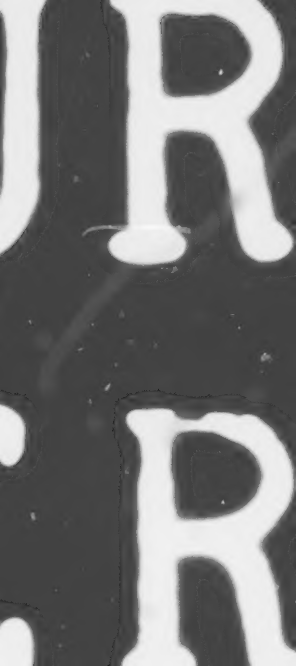
The selection of an appropriate and cost-effective sludge dewatering alternative requires the consideration and evaluation of the various factors relating to a specific case. An overall approach is suggested here, although many of the factors involved are quite specific to a given situation and their importance may be weighted differently from plant to plant.

Table 1 outlines the procedures for developing and selecting an overall sludge dewatering plan. The initial task is to establish the sludge quantity and characteristics, either from data from an existing system or using the design basis for a yet-to-be-built treatment plant. Consideration of future loads, present sludge handling practices, if any, average and maximum sludge production rate, and the effect of storage on sludge handling rates are included. Potential sludge reduction alternatives such as inplant recovery of waste constituents, or a digestion step prior to dewatering would be considered at this point to identify feasibility on a preliminary basis.

An evaluation of potential ultimate disposal alternatives will provide information on the required characteristics of the solids to be disposed, and consequently, dewatering requirements. Availability, cost, and feasibility of the use of land sites for possible land application or landfill should be determined. The possible need to reduce sludge or landfill should be determined. The possible need to reduce sludge quantities to a minimum by incineration due to unavailability of landfills or high hauling costs requires an early evaluation.

Bench-scale tests are conducted on potential dewatering alternatives at this point, and using these results along with general typical information, as is shown in Tables 2 and 3, a preliminary screening and consideration of sludge dewatering alternatives can be made. Available data from similar installations can be evaluated to aid in developing sizing and costs, and to evaluate extended operational performance and operating cost factors, particularly for the newer and/or different types of specific equipment available. State and local regulations on land disposal and landfills are also considered in the screening process.

At this point a decision usually can be made, and one or two sludge dewatering alternatives selected for detailed evaluation. Although various activated sludges generally have the same characteristics, they also have differences which can effect the performance of dewatering systems. It is therefore advisable to perform pilot-scale tests, when possible, to demonstrate performance and provide confirmation of preliminary bench-test sizing parameters. In some cases, side-by-side comparisons of different sludge dewatering systems and different equipment may be desirable for comparison of performance. Extensive testing,



G

S

TABLE 1. PROCEDURES FOR DEVELOPING AND SELECTING A SLUDGE DEWATERING PLAN

1. Define sludge quantity and characteristics
    - A. Average – maximum quantities
    - B. Effect of sludge storage on rates
    - C. Identify potential sludge reduction alternatives
2. Define ultimate disposal alternatives and sludge solids requirements
3. Bench scale evaluation of alternatives compatible with probable ultimate disposal
4. Preliminary sizing and capital and operating costs evaluation of alternatives
5. Pilot scale evaluations of indicated system(s) for final design parameters and performance confirmation
6. Final design sizing of dewatering system(s)
7. Final development of overall sludge handling plan(s)
    - Capital cost estimate
    - Operating cost estimate
    - Financial strategies
8. Selection of overall plan and required equipment

however, is not always necessary, particularly for smaller installations where the effect of conservative design parameters would have only slight effect on the final cost of the dewatering system. An example of this would be the case where the minimum standard size equipment capacity exceeds the design sludge quantity.

With process design and performance parameters established, the selected dewatering alternatives are sized, based on sludge quantities, full-size equipment capabilities, and operational requirements. At this point, with characteristics of the sludge cake known, further evaluation of the ultimate disposal alternatives available may be made. Additionally, the cost of the dewatering step can be compared with identified potential sludge reduction alternatives, and a decision on reduction steps may be made. Following finalization, the proposed total sludge handling plans are reviewed and capital and operating cost estimates prepared. The type of dewatering equipment can be selected and quotes for specific equipment obtained for an economic analysis of the sludge handling plans. Factored into these cost analyses would be the company's financial strategies for dealing with capital and operating expenditures for pollution control.

Finally, with all relevant factors considered, the overall sludge handling scheme and the dewatering alternative can be selected.

Table 2 presents performance data for four types of mechanical dewatering equipment. The results shown are based on literature data and actual test data developed in several studies conducted by Hydroscience. The belt filter press and centrifuge use polymers for sludge conditioning. Although polymers generally constitute a major part of the sludge dewatering costs, they are very effective, and eliminate the bulk chemical storage, handling, and feed systems generally associated with the filtration systems. The cake solids and recovery are comparable for the belt filter press and vacuum filter; somewhat lower cake solids and capture are noted for the centrifuge, while the pressure filter produces the highest cake solids, and achieves virtually complete solids capture. Table 2 shows the remaining moisture content based on sludge solids, a significant consideration particularly if the sludge is to be incinerated. It also gives the approximate volume of cake solids per ton of sludge solids, which must be figured into sizing landfills and determining haulage costs.

TABLE 2. PERFORMANCE ESTIMATES FOR MECHANICAL DEWATERING OF WASTE ACTIVATED SLUDGE

Dewatering device	Chemical	Dosages*	Approx.† chemical cost	Unit sizing criteria	Cake solids conc. (percent)	Approx. % solids recovery	Kg water‡ remaining per kg dry sludge solids	Cubic meters of cake per ton dry sludge solids
Belt filter press	Polymer	2.5-10	12-45	115-180 kg per hour per meter of belt width	10-20	90	6.7	6.6
Solid bowl centrifuge	Polymer	0-10	0-45	135-225 kg per hour per 56 cm diameter × 1.7 m long machine	6-10	50-90	11.5	12.4
Vacuum filtration	$FeCl_3$ $Ca(OH)_2$	60-100 200-400	20-35	5 to 15 kg per hour/m^2	12-18	93	7.8	8.9
Recessed plate	$FeCl_2$	60-200	28-66	0.5 to 1.0 kg per hour/m^2	24-30	99	4.1	5.3
Pressure filter	$Ca(OH)_2$ Precoat	200-500 25		25 mm thick cake 2 to 4 hours cycle				

* Dosage = kg of chemical/metric ton of dry sludge solids.

† Cost = dollars/metric ton of dry sludge solids.

‡ Based on average cake solids

$FeCl_3$ – $165/ton, polymer – $4.40/kg
Lime – $55/ton, precoat – $220/ton.

Table 3 presents performance and general design parameters for land alternatives for sludge dewatering. These techniques typically do not require chemical conditioning, and rely primarily on draining and evaporation for dewatering. The importance of general climatic conditions for design, and local weather conditions for operation is obvious. Normally use of sand beds requires return of the drainage to the treatment facility. With drying lagoons and high-rate land applications, however, evaporation rates, soil conditions, and leachate quality will determine the necessity of returning supernatant and leachate to treatment. Leachate is usually not returned from low-rate land application in which nutrients are incorporated into a harvested crop and other constituents such as heavy metals are adsorbed and retained in the soil. The 2-step operation associated with drying beds and lagoons—sludge application and sludge removal after dewatering—is indicated by the range of time between applications. Since with land application the sludge is incorporated into the soil, that process is also considered an ultimate disposal scheme. Table 3 shows approximate cake solids for each alternative and relative land requirements, based on an average loading for 1 ton per day waste sludge solids, are presented.

Table 4 presents a cost comparison for mechanical dewatering systems. The equipment selected was based on the unit sizing criteria, Table 2, and standard-sized manufacturers units. Equipment costs, which include chemical storage and feed systems, represent an approximate average estimate for the type of equipment indicated, and are probably within ± 20 percent of current quoted costs.

TABLE 3. PERFORMANCE AND GENERAL DESIGN CRITERIA FOR LAND ALTERNATIVES FOR SLUDGE DEWATERING

System	Sizing criteria[*]	Land required acres/ton/d[†]	Cake sludge solids
Open sand drying beds	1. No chemicals – 50 to 100 $kg/m^2/yr$, 4 to 6 weeks between applications	1.2	40 to 50 percent
	2. Polymers – up to 400 $kg/m^2/yr$, 1 to 3 weeks between applications – drainage returned	0.4	40 to 50 percent
Covered sand drying beds	No chemicals – 100 to 200 $kg/m^2/yr$, 1 to 3 weeks between applications – drainage returned	0.7	40 to 50 percent
Drying lagoons	30-50 $kg/m^3/yr$, 0.5 m to 1.25 m depth 3 to 5 months drying time, supernatent returned lining may be required, 2 or more lagoons used	14.3	25 to 40 percent
Land applications	1. Crop-nutrient uptake–1.25 to 5.0 $kg/m^2/yr$	30	Sludge incorporated into soil
	2. Noncropland, drainage returned, up to 25 $kg/m^2/yr$ storage during wet or cold seasons may be required	4.5	

[*] Dry sludge solids basis.

[†] Average sizing used.

TABLE 4. COMPARISON OF MECHANICAL DEWATERING ALTERNATIVES (ESTIMATED CAPITAL AND OPERATING COSTS BASED ON 1,100 METRIC TONS/YR WASTE ACTIVATED SLUDGE SOLIDS CONTINUOUS OPERATION – 300 DAYS/YR)

Equipment	Equipment costs ($\$ \times 10^3$)[*]	Total installation cost[†] ($\$ \times 10^3$)	Operating power (hp)	O/M labor[‡] (h/yr)	O/M costs[§] (\$/ton dry (sludge solids)
One 1-meter belt filter press	100	220	10	365	20-55
One – 22" ϕ × 66" solid bowl centrifuge	130	290	50	2,000	35-80
One – 300 ft^2 vacuum filter	135	320	50	4,200	65-90
One – 90 ft^3 capacity pressure filter	200	450	20	7,000	100-145

[*] Equipment costs approximate – vary with manufacture; includes major chem feed equipment.

[†] Total installation – 2 to 2.5 times equipment costs; building and utilities not included.

[‡] Labor requirements from reference 7.

[§] O/M costs include power at 3¢/kWh, labor at $10/h, spare parts at 2 percent equipment cost, and chemical costs in Table 1. Amortization of equipment and final disposal of sludge not included in O/M costs.)

TABLE 5. COMPARISON OF LAND DEWATERING ALTERNATIVES (ESTIMATED) CAPITAL AND OPERATING COSTS BASED ON 1,100 METRIC TONS/YR WASTE ACTIVATED SLUDGE SOLIDS)

System	Capital[*] costs ($ × 10^3)	O/M labor (h/yr)	O/M Costs[‡] ($/ton/dry sludge solids)
Sand drying beds 4 acres open	420	6,600	45-80
Drying lagoons 1 million gallons, 7.5 acres	120	150	2-6
Land application/ crop – 110 acres	300	3,100	30-45
High loading 20 acres[†]	175	2,100	20-35

[*] Land costs do not include pumping and transmission to and recycle from land site.

[†] Includes underdrains.

[‡] O/M for pumping and transmission costs not included – variable site specific. (Costs for ultimate disposal of sludge removed from drying beds or drying lagoons not included.)

Total installation cost is based on factoring the equipment costs and includes engineering, contractor costs, foundations, controls, and associated piping and electrical work. The belt filter press, solid bowl centrifuge, and vacuum filter capital costs are comparable, whereas the pressure filter costs are somewhat higher.

The chemical feed systems required for the bulk chemicals used with vacuum filtration and pressure filtration affect capital costs. Although advances in polymer chemistry and use of polymers for conditioning in some cases have replaced these bulk chemicals, the nature of activated sludge has generally required the bulk chemicals for filter application.

Chemical costs are the major part of the operating and maintenance costs; however, power and labor are significant particularly for the filtration processes. It may be noted that labor costs for pressure filters may vary considerably with the type of equipment and degree of automation. All of these estimates would require final evaluation in a specific case. As noted on the table, costs for final sludge haulage and disposal are not included. These costs are site specific and can be significant to the extent that they will influence the final selection of the dewatering alternative.

Table 5 compares relative costs for land dewatering alternatives. Sand-drying beds require substantially less area, but they are structured units. Consequently, capital costs are significantly higher for these than for earthen drying lagoons with liners or for the preparation of relatively level, lightly vegetated land on which to spread or inject sludge. The labor requirements reflect the frequency of removing sludge from the drying beds and lagoons, and the application of the sludge in the land application schemes.

It should be noted that land costs, if any, or special land preparation costs, as well as the costs for construction and operation of pumping and transmission facilities to transfer sludge to the dewatering site and the return of leachate or supernatant are not included, since these costs are highly site specific and can vary substantially. They should, however, be included in the final cost evaluation of these alternatives for a specific case. The costs presented for these alternatives are somewhat less precise than those developed for the mechanical dewatering systems.

CONSIDERATIONS FOR SELECTION OF A DEWATERING PROCESS FOR EXCESS ACTIVATED SLUDGE

As previously mentioned, selection of a dewatering alternative is site specific and to a large extent depends upon the ultimate disposal technique. Nevertheless, certain generalizations concerning the various techniques can be made based on the information and data generated and summarized in this paper.

Land application that includes ultimate disposal appears to be a cost-effective solution to dewatering and disposal, given two provisions. Adequate suitable land must be available, and the various concerns with respect to designing for reasonable loading rates, i.e. the handling of runoff and lechate and nonobjectionable aesthetics, must be adequately addressed.

Lagoon drying is a low-cost dewatering solution, but is more susceptible to problems with odors and unsightly conditions than land applications. Also periodic sludge removal to ultimate disposal is required with this method.

Sand beds, while demanding less land than the other land alternatives, are high in both capital cost and labor cost due to frequent sludge removal. Here, also, the sludge must be hauled to ultimate disposal.

As with all equipment, the machinery for mechanical dewatering alternatives is subject to breakdown, and the need for repairs and replacement requires consideration. Numerous manufacturers offer various types of equipment with different features and costs. Selection of the equipment best applicable to a specific case requires an evaluation of these aspects based on mechanical design and operating experience of the equipment being considered.

Of the mechanical dewatering systems, the relatively new belt filter press equipment appears to be the most cost effective system to produce a sludge cake suitable for disposal. The pressure filter is a probable alternative in the event incineration or long-distance hauling is required. However, the desirability of charging an incinerator with the large quantities of ferric chloride and lime used for conditioning, and of subsequently disposing of significant quantities of ash, requires consideration. Use of the vacuum filter for dewatering activated sludge appears to be less cost effective than the belt filter press and therefore would probably no longer be considered in most cases for this type application.

Dewatering with centrifuges does not produce as dry a cake as the other alternatives; yet centrifugation may be applicable in a sludge handling plan wherein chemical use is minimized, and cost benefits are achieved by producing a thickened, semifluid sludge for subsequent handling by digestion, heat treatment, or land disposal.

REFERENCES

1. National Council of the Paper Industry for Air and Stream Improvement, "A Pilot Plant Study of Mechanical Dewatering Devices Operated on Waste Activated Sludge," Technical Bulletin No. 288, November 1976.
2. U.S. Environmental Protection Agency, *Process Design Manual for Sludge Treatment and Disposal,* EPA 625/1-74-006, October 1974.
3. W. E. Garrison, J. F. Stahl, L. Tortorici, and R. P. Micle, "Pilot Plant Studies of Waste Activated Sludge Processing," *J. Water Pollution Control Federation,* Vol. 50, No. 10, p. 2374, October 1978.
4. G. T. O'Hara, S. K. Raksit, and D. R. Olsen, "Sludge Dewatering Studies at Hyperion Treatment Plant," *J. Water Pollution Control Federation,* Vol. 50, No. 5, p. 912, May 1978.
5. E. Cole, S. Corr, and J. Albert, "Sludge Dewatering in Textile Plants," *Industrial Wastes,* January/February 1977.
6. National Council of the Paper Industry for Air and Stream Improvement, "Full Scale Operational Experience With Filter Presses for Sludge Dewatering in the North American Pulp and Paper Industry," Technical Bulletin No. 299.
7. U.S. Environmental Protection Agency, *Operators Manual - Sludge Handling and Conditioning,* EPA 430/9-78002, February 1978.
8. R. V. Villiers and J. B. Farrell, "A Look at Newer Methods for Dewatering Sewage Sludges," *Civil Engineering ASCE,* December 1977.
9. P. N. Cheremisinoff, "Sludge Handling and Disposal – A Special Report," *Pollution Engineering,* January 1976.
10. J. A. Bell, R. Higgins, and D. G. Mason, "Dewatering: A New Method Bows," *Water and Wastes Engineering,* April 1977.

11. American Society of Civil Engineers, *Wastewater Treatment Plant Design,* ASCE Manual No. 36, 1977.
12. U.S. Environmental Protection Agency, "Proceedings of the Joint Conference on Recycling Municipal Sludges and Effluents on Land," 1973.
13. J. A. Mueller, "Land Disposal of Sewage Sludge — State of the Art," Hydroscience Internal Research Report, September 1976.
14. G. J. Bisjak and A. E. Becher, "Wausau Solves Dual Problems by Using Filter Press," *Water and Wastes Engineering,* February 1978.
15. A. E. Dembitz, "Belt Filter Presses: A New Solution to Dewatering," *Water and Wastes Engineering,* February 1978.
16. U.S. Environmental Protection Agency, "Costs of Wastewater Treatment by Land Application," EPA 430/9-75-003, June 1975.

RATIONALE FOR SLUDGE MANAGEMENT IN A WASTEWATER TREATMENT PLANT

P. Aarne Vesilind*

Abstract

Sludge management in wastewater is expensive and can be troublesome. This paper presents three basic "laws" for sludge management which, it is suggested, can reduce costs and problems with sludge handling. These three guidelines are:

1. *Don't hold sludges,*
2. *Don't mix sludges, and*
3. *Don't recirculate sludges.*

If these laws are followed, dewatering costs can be reduced, odor problems alleviated, and environmentally acceptable ultimate disposal of the sludge facilitated.

INTRODUCTION

A wastewater treatment plant exists for the purpose of producing an essentially clear effluent that can be discharged into the environment without adverse impact. The design engineer and plant operator therefore are mostly concerned with the liquid processing within the plant, and solids management becomes important only when the plant malfunctions. Often, these upsets can be avoided by following a few fairly simple guidelines for sludge management within a plant. Malfunctions, from the operator's viewpoint, are either effluent quality problems forcefully brought to his attention by State or Federal inspectors, or sludge problems which usually consist of having too much of a bad thing and nowhere to put it. The objective of this paper is to focus on the latter problem—sludge handling—and to present some general guidelines, which in the author's opinion will reduce the costs and headaches associated with wastewater sludge management.

THREE LAWS OF SLUDGE MANAGEMENT

Stated concisely, these laws of sludge management are:

1. Don't hold sludges,
2. Don't mix sludges, and
3. Don't recirculate sludges.

As is the case with any generalities, these are not always applicable. However, they have been found to be true at enough plants to warrant discussion.

Holding Sludge

Holding sludge (saving it, storing it, etc.) is usually the doing of a plant operator, and the procedure is often dictated by the vagaries of the labor force. It should nevertheless be the aim of an operator not to hold sludge before a subsequent operation such as dewatering. Although this principle seems to be especially applicable to raw primary sludges, the holding of digested sludge (and the resulting cooling) has been shown to cut the capacity of mechanical dewatering to one third of the original (ref. 1).

One clear outward sign of impending trouble is bubbling primary clarifiers, due to holding raw sludge in the primary clarifiers, and the subsequent gas formation within the settled raw sludge. This will decrease the efficiency of solids removal, as well as place an extra load on the alkalinity of the anaerobic digesters. Sludge should be pumped from the primary clarifiers at sufficiently frequent intervals so as to avoid septicity.

Mixing Sludge

The second axiom, "Don't mix sludges," is violated by both design engineers and plant operators. For example, experience seems to indicate that the discharge of excess waste activated sludge to the head of the plant results in deterioration of the primary clarifier performance, significantly increases the volume of sludge pumped, and necessitates more frequent pumping due to increased septicity problems.

---

*Associate Professor of Civil Engineering, Duke University, Durham, NC.

It has been known for some time that when a raw primary sludge is mixed with waste activated sludge, the mixture assumes many of the undesirable characteristics of waste activated sludge. It is, for example, very difficult to mechanically dewater a 1:1 mixture of raw primary and waste activated sludge. The excellent dewaterability of raw primary sludges is sacrificed when mixed with secondary sludges.

It is, however, necessary to achieve the highest solids concentrations possible before a process such as anerobic digestion, since the governing operational parameter in anaerobic digestion is solids retention time. One means of achieving this has been to blend the raw primary and waste activated sludges in a gravity thickener (ref. 2). This has at times caused operational problems such as floating sludge and odors, mainly due to the oxygen-starved nature of the sludges. A more reasonable solution seems to be the gravitational thickening of primary sludges and the use of floatation thickeners for aerobic secondary sludges, with blending following the separate thickening operations and then subsequent anaerobic digestion. In plants where this type of scheme has been instituted, the solids dewatering has improved markedly and operational problems have been reduced. (ref. 3)

Another example of improved operation by not mixing sludges is the scheme of using anaerobic digestion for raw primary sludge only, and employing aerobic digestion for the waste activated sludge. These stabilized sludges can then be blended and dewatered at a cost significantly lower than the alternative of mixing prior to stabilization (ref. 3).

Recirculating Sludge

The final rule, "Don't recirculate sludges" is probably the most difficult of the three laws to promote, since the recirculation of various sundry process streams to the head of the plant is almost a knee-jerk reaction for design engineers. These streams can, however, impose a significant excess solids load on the process.

Consider a 10 mgd plant which has a gravity thickener for the primary and waste activated sludges (5,080 kg/day at 4 percent solids and 7,130 kg/day at 1 percent solids, respectively) and a centrifuge to dewater the anaerobically digested sludge. The solids recovery of the thickener and centrifuge is 90 percent and 80 percent respectively, and the supernatant from the secondary digester has a solids concentration of 2 percent with digester influent and effluent solids of 5 percent and 8 percent respectively. What fraction of the total solids load on the treatment plant is produced by the return flows from the thickener, centrifuge, and secondary digester?

1. Thickener overflow, with 90 percent solids capture, is

$$0.10\ (5{,}080\ \text{kg/day} + 7{,}130\ \text{kg/day}) = 1{,}221\ \text{kg/day.}$$

2. The total solids flow into the anaerobic digester is thus

$$0.9\ (5{,}080\ \text{kg/day} + 7{,}130\ \text{kg/day}) = 10{,}989\ \text{kg/day.}$$

Of this solids load, assume 20 percent is lost (gas plus dissolved solids) so that the digester effluent solids (supernatant + underflow) is 8,791 kg/day, while 2,198 kg/day is lost in the digestion. Mass balance on the digester in terms of the sludge solids is

$$\begin{aligned}\text{inflow} &= \text{underflow} + \text{supernatant} \\ &\quad + \text{loss in digestion} \\ 10{,}989\ \text{kg/day} &= x\ \text{lb/day} + y\ \text{lb/day} \\ &\quad + (-2{,}198\ \text{kg/day}).\end{aligned}$$

The mass balance in terms of total liquid is

$$\text{inflow} = \text{underflow} + \text{supernatant}$$

$$\frac{10{,}989}{0.05}\ \text{kg/day} = \frac{x}{0.08}\ \text{kg/day} + \frac{y}{0.02}\ \text{kg/day.}$$

Solving the two simultaneous equations:

x = solids in underflow
= 2,930 kg/day
y = solids in supernatant
= 3,663 kg/day.

3. The centrifuge operates at 80 percent solids capture on the underflow, so that the concentrate contains

$$0.2\ (2{,}930\ \text{kg/day}) = 586\ \text{kg/day}.$$

The total contribution of recycled solids is thus

$$1{,}221\ \text{kg/day} + 3{,}663\ \text{kg/day} + 586\ \text{kg/day} = 5{,}470\ \text{kg/day}.$$

Since the plant influent carries 8,527 kg/day, the recycled solids increase the total solids load on the plant by

$$\frac{12{,}060}{18{,}800} \times 100 = 64\ \text{percent.}$$

In addition to the total magnitude of the additional solids load on the plant, the types of solids recirculated are almost exclusively the fine, difficult to handle solids. More than one treatment plant operator has found himself inundated with these fine solids, at the eventual expense in treatment efficiency. The only solution in such cases is to clean the plant out. In the design and operation of a plant, therefore, one should not recirculate solids if at all possible. In the example above, the 2 percent solids supernatant clearly has an impact on operation, and the practice of supernatant withdrawal is of highly questionable value. Many operators prefer to dewater all of the sludge, and to do this at a high rate of solids recovery, recognizing that this investment is highly profitable for future good plant operation.

CONCLUSION

Efficient and effective operation of wastewater treatment facilities requires careful consideration of sludge handling practices. It is suggested that three practical guidelines which could assist in the management of wastewater sludges are: don't hold sludges; don't mix sludges; and don't recirculate sludges.

REFERENCES

1. P. I. Vermehen, "Chemical Removal of Nutrient Salts from Plant Effluent," Sixth Nordic Symposium on Water Research, Copenhagen, 1978.
2. W. N. Torpey, "Concentration of Combined Primary and Activated Sludges in Separate Thickening Tanks," *Proc. ASCE 80,* No. 443, September 1954.
3. U.S. Environmental Protection Agency, *Process Design Manual for Sludge Treatment and Disposal,* U.S. EPA Technology Transfer, 625/1-74-006, Washington, DC, 1974.

TEXTILE SLUDGE TREATMENT AND DISPOSAL

David H. Bauer,* John P. Woodyard,† Stephen P. Shelton‡

Abstract

Increasing quantities of wastewater treatment sludge generated by more stringent water and air quality standards and pending regulations to control the disposal of hazardous wastes have focused new emphasis on possible solutions to the problem of sludge disposal. Disposal alternatives currently applicable to the textile industry include lagoons landfilling, land farming, incineration, and wet air oxidation. Current indications are that landfilling and land farming disposal will predominate in the future, subject to pending regulations. Incineration and wet air oxidation may be used on special problem wastes, such as residuals generated by reverse osmosis treatment of wastewaters.

INTRODUCTION

Recent estimates indicate that approximately 39,000 metric tons (dry weight) (43,000 tons) of sludge are currently generated annually by the textile industry, and this is projected to increase to 167,000 metric tons, (164,000 tons) annually by 1983 (ref. 1). Thus, adequate sludge disposal is becoming a major concern in the industry, especially in EPA Regions I and IV where approximately 65 percent of all textile industry sludge is generated.

The disposal of sludge, including that of the textile industry, has received increasing emphasis in recent years, primarily as a result of increasing sludge generation from water reuse and pollution control systems. With passage of the Clean Water Act of 1977, EPA responsibilities for industrial point source effluent controls have been specifically defined to include toxic pollutants, conventional pollutants, and nonconventional pollutants. Control of 65 classes of toxic compounds is incorporated in Section 307(b) as best available technology (BAT) effluent limitations for 21 "heavy" industry categories, including the textile industry. Similar revised authority governing conventional and nonconventional pollutants is also included. Thus, increased textile sludge generation is anticipated, although the magnitude of the increase will depend on the specific limitations adopted and the extent to which pretreatment requirements are imposed on textile plants.

In addition, the Resource Conservation and Recovery Act (RCRA) of 1976 has expanded EPA authority governing sludge disposal. Specifically, Section 3001 (criteria, identification, and listing of hazardous wastes) gives EPA authority to define hazardous wastes. The "status draft" of Section 3001 regulations includes a list of processes considered to generate hazardous waste, including six textile processes. Thus, EPA regulations authorized by Subtitle C of RCRA will be applicable to a significant portion of the sludge generated by the textile industry.

In an effort to address future sludge disposal concerns, this paper focuses on treatment and disposal methods currently in very limited use but which appear to have promising applications.

TEXTILE INDUSTRY SLUDGE CHARACTERISTICS

Before appropriate treatment and disposal technology can be selected, the sludge characteristics must be determined. First, data on physical characteristics is needed, such as specific gravity, solids concentration, settling properties and particle size and distribution. Subsequently, chemical properties such as fuel value, fertilizer value, food value, and electrophoretic properties, as well as specific chemical characteristics (especially toxins), should be evaluated. Lastly, biological characteristics such as carcinogenicity, mutagenicity, and enzymes may need to be evaluated.

It should be noted that characterization of sludge can be a complex problem with an ex-

---

*Project Manager, SCS Engineers, Reston, VA.
†Vice President, SCS Engineers, Long Beach, CA.
‡Associate, SCS Engineers, Columbia, SC.

Preceding page blank

pensive solution. Thus, the identifying characteristics of interest need to be specified relative to the methods of treatment or disposal that initially appear most feasible. For example, if a sludge is to be thickened in a gravitational thickener, a characteristic of primary interest would be settling; whereas if the sludge is to be used as a fertilizer, nutrients and toxic constituents would be of primary interest.

Textile industry sludge characteristics are the subject of another paper scheduled for this symposium, and are therefore discussed only briefly here. Concentrations of selected constituents of general interest in dry sludge from six categories of textile mills are presented in Table 1. Heavy metal concentrations range from 2.5 to 2,370 mg/kg on a dry weight basis, and the total chlorinated organics content is between approximately 0.1 and 65 mg/kg. Of the five heavy metals shown, cadmium concentrations were consistently the lowest (always <17 mg/kg) and zinc concentrations the highest (>550 mg/kg) for five of the six categories (ref. 1).

Sludge produced from treatment of textile industry wastewater is either retained in a treatment system, such as a lagoon or pond, or wasted from the system, as in an activated sludge treatment unit. The solids content of wasted sludge ranges from 2 to 10 percent, depending on the industry category and the method of disposal used. The solids content of retained sludge ranges from 1 to 10 percent (ref. 1).

OVERVIEW OF SLUDGE MANAGEMENT

Industrial sludges are typically disposed in sanitary and chemical landfills, in lagoons or ponds, in deep wells, or by incineration (ref. 2). Some sludges are recycled or stockpiled and some sludges are disposed by ocean dumping. In addition, sludges are sometimes disposed by open dumping. Incidences of air, ground, and surface water pollution from improper land disposal of industrial wastes have been reported (ref. 3). Although adequate technology for industrial sludge management reportedly exists, this technology is costly (approximately 5 to 20 times as expensive as current unacceptable practices such as uncontrolled land dumping or ocean disposal) (ref. 4).

In the textile industry, sludge treatment may involve dewatering, wet air oxidation, incineration, stabilization, or fixation, but no treatment prior to disposal is currently typical of the industry. Sludge disposal in lagoons, and to a lesser extent landfills, is also typical, al-

TABLE 1. CHEMICAL CHARACTERISTICS OF SELECTED TEXTILE INDUSTRY SLUDGES

Constituent	Categories/mg/kg of dry sludge[§]					
	A	B	D	E	F	G
Cadmium	1.2	.7	4.4	4.5	10	2.5
Chromium	19	267	1,196	33	112	31
Boron	26	170	36	52	110	25
Zinc	106	1,130	2,370	550	1,790	1,505
Copper	16	117	652	410	211	264
Total Chlorinated Organics	13	0.11	15.2	64.7	26.2	40.1

[§] Values presented are averages for each of the following categories:

A - wool scouring
B - wool fabric dyeing and finishing
D - woven fabric
E - knit fabric
F - tufted carpet dyeing and finishing
G - yarn and stock dyeing and finishing

Source: Reference 1.

though dumps and land spreading are sometimes used.

Sludge dewatering is currently practiced at relatively few textile plants, but is anticipated to be used more as sludge volumes increase and disposal requirements become more stringent. Wet air oxidation has been used in at least one textile plant for wastewater sludge treatment, but has proven uneconomical to operate due to the small volumes of sludge generated. Incineration is used to incinerate process wastes at a few textile plants, but not sludge, presumably due to the relatively high cost (ref. 1).

In the future, the use of incineration and/or wet air oxidation may increase for the treatment of wastewater treatment residuals. In particular, residuals produced by reverse osmosis (RO) treatment of textile wastewaters present a difficult disposal problem that may only be adequately solved with these methods of treatment. Similarly, stabilization and fixation will likely be used increasingly to enable sludge management to comply with applicable regulations.

Textile plant wastewater treatment systems frequently include aerated lagoons. In many instances, the sludge accumulation rate is slow enough that sludge wasting is required very infrequently. In those plants that routinely waste sludge, sludge disposal is frequently handled by the textile plant, either onsite or offsite. Thus, lagoons and landfills are the most common disposal sites, with land spreading and dumping used occasionally.

The methods of sludge disposal used in the future will likely depend in large part on pending Federal hazardous waste regulations and solid waste disposal criteria. It is anticipated that use of offsite disposal facilities, such as lined lagoons and landfills with leachate collection and treatment (if necessary) and land spreading will become increasingly common.

SLUDGE TREATMENT

Selection of a sludge treatment method obviously depends on the method of disposal. Currently, lagoons are the most common disposal method. Thus, sludge treatment in the textile industry is atypical. However, it is anticipated that landfill disposal will be used increasingly. Stabilization and chemical fixation are two methods of treatment used in other industries to facilitate landfill disposal, and which appear to have promising applications in the textile industry. The following discussion is limited to these two techniques.

Stabilization

Raw sludges can be stabilized prior to ultimate disposal to increase the number of acceptable disposal options. By far the most common sludge stabilization technique is anaerobic digestion. Many variations of this technique have been used from septic tanks through completely mixed heated digestors; however, sludge toxicity can be a problem regardless of digestor configuration. This problem is often encountered in industrial waste treatment and would likely be a problem for a significant number of textile waste sources.

Aerobic sludge digestion has drifted in and out of favor over the past 20 years. The process is generally less affected by toxins than anaerobic digestion. However, the energy costs are high. Because of increased emphasis on energy conservation and high costs, it is unlikely that use of aerobic sludge stabilization will become as common for textile sludges.

Lime addition is another technique which has long been used for sludge stabilization, since it can increase sludge pH until most biological life is destroyed. Quicklime (CaO), also has the ability to dewater sludge through a hydration reaction. This has the advantage of avoiding oxidation-reduction reactors which can potentially produce hazardous byproducts. In the South, where many textile operations are located, an inexpensive lime source, marl, can often be mined onsite for use in sludge dewatering.

The primary disadvantage of lime stabilization is that the effects are short-lived. It has been shown by Paulsrud (ref. 5) that lime sludges are not chemically stable and that it is impossible to maintain a high pH even with very high lime dosages. Chemical and/or biological action eventually seems to bring the pH down and with that odors return.

Oxidants such as chlorine have also been used for sludge stabilization; however, the problems of recent concern regarding chloramines will probably discourage use of chlorine for future applications.

Lagooning of sludges by industry is a long-practiced stabilization technique, and is certainly the most common method currently used in the textile industry. This is not to say that the primary purpose of most sludge lagoons in the textile industry is stabilization, since most are designed either as temporary holding basins or as a means for ultimate sludge disposal. However, some lagoons are designed as digestors. The requirement for thorough digestion in a lagoon is generally about 3 years detention time, 1 of the years being required for resting without sludge addition. It should be apparent that such lagoons are practical only in low-density areas where inexpensive land is available.

Fixation

An increasing number of industries are favoring dry disposal of their waste sludges. In addition to the advantages in disposal as a solid, transportation and handling are also enhanced.

Many sludges are not readily dewatered through conventional mechanical means, and as such may not possess adequate strength for use as fill material. The physical or chemical fixation of these materials can provide the added strength and reduced permeability desirable for landfill disposal. Physical fixation, which may only involve the addition of dry materials to increase the solids content, is sometimes adequate if the disposal site is reasonably secure and land reclamation is the primary concern. On the other hand, chemical fixation gives the sludge both a predictably high load-bearing strength and a low permeability. In no case do these sludge treatment processes attempt to remove contaminants from the material; they simply serve either to improve physical properties or reduce contaminant mobility.

The predominant use of fixation to date has been in the utility industry. Because textile plants do not necessarily have the large quantities of fly ash and bottom ash available to mix with waste sludges, chemical fixation may be the best available alternative for dry disposal. A recent study of FGD sludge fixation technology identified a total of 16 companies which offer sludge fixation processes or services. These companies are displayed according to their experience in Table 2 (ref. 6).

Fixation companies typically offer not only a fixation process itself, but may also offer engineering and operating services to their client. Of the 16 companies listed in the table, two companies have actively and successfully marketed their services to utilities for FGD sludge management. These companies are IU Conversion Systems, Inc. (IUCS) and the Dravo Corporation. Both of the processes are proprietary in nature, involving the addition of at least one material typically foreign to power plant operations.

IUCS markets a system of FGD sludge fixation using lime and fly ash. In the IUCS process, vacuum-filtered sludge is mixed with fly ash and lime in a pug mill. Dry fly ash is added in proportions varying from 50 to 100 percent of the dry sludge weight. Lime is added at a rate of 3 to 4 percent. IUCS calls the finished material Poz-O-Tec.

Disposal of the sludge is accomplished by landfilling. The mixture is controlled to optimize compaction properties. Pozzolanic reactions between the lime and fly ash result in a significant increase in load-bearing strength after the material has cured. Compared to untreated sludge, Poz-O-Tec has lower moisture content (15 to 25 percent), much reduced permeability (10^5 to 10^6 cm/sec) and compressibility, as well as increased bulk density. As an alternative to landfill disposal, Poz-O-Tec can be used as a structural construction material. Possible uses include road bases; pond, landfill, or reservoir lining; concrete or asphalt aggregate; and artificial reefs.

Mechanical compaction of Poz-O-Tec is required to obtain the optimum strength and minimum permeability. If the compacted material is disturbed it will undergo a decrease in density. Since the in situ Poz-O-Tec material is unsaturated, disturbances will not reslurry the material.

The Dravo fixation process (patented) involves the addition of Calcilox, a proprietary material manufactured from blast furnace slag, to the sludge. Calcilox is a basic, pozzolanic additive which improves sludge handling characteristics and disposal properties.

Three treatment/disposal schemes are possible using Calcilox as a fixation agent: perma-

TABLE 2. COMPANIES PROVIDING COMMERCIAL FIXATION OR DISPOSAL SERVICE

Companies	Commercial experience with other residues	System specific for FGD sludge	Full-scale experience with FGD sludge	Bench scale with FGD sludge	Field tests with FGD sludge
Aerojet Liquid Rocket	Extensive	Yes	None	Yes	None
Amax Resource Recovery Systems, Inc.	Extensive	Yes	None	Yes	None
American Admixtures Company (Formerly Chicago Flyash)	No	Yes	Will County (140 Mw)	Yes	Will County
Anefco Company	Extensive	Yes	None	None	None
Chemfix	Extensive	Yes	None	Yes	Shawnee, Will County
Chem-Nuclear Systems, Inc.	Extensive	Yes	None	None	None
Dravo Corporation	Limited	Yes	Bruce Mansfield (1,650 Mw)	Extensive	Shawnee, Mohave, Phillips
Environmental Technology Corp.	Limited	Yes	None	Yes	None
IUCS	Extensive	Yes	Phillips (400 Mw) Elrama (500 Mw) Petersburg (515 Mw) Conesville (403 Mw)	Extensive	Shawnee, Phillips, Mohave, Elrama, Four Corners
Marston Associates	No	Yes	None	Yes	St. Clair
Ontario Liquid Waste Diposal Limited	Extensive	Yes	None	Yes	Mississauga
TUK, Inc.	Extensive	Yes	None	None	None
Sludge Fixation Technology, Inc.	None	Yes	None	Yes	None
United Nuclear Industries	Extensive	Yes	None	Yes	None
Wenran Engineering Corporation	Not known	Yes	None	Yes	Non
Werner Pfleiderer Corporation	Extensive	Yes	None	None	None

Source: Reference 6.

nent ponding; temporary ponding; and direct landfilling. Permanent ponding involves adding Calcilox and hydrated lime to the sludge before pumping the mixture to a holding pond. The hydrated lime is required to adjust the pH above 10.5. Calicox is added at the rate of 5 to 10 percent of sludge solids. Curing is completed in approximately 30 days. Supernatant is then returned to the FGD system.

Where large tracts of land are not available, temporary ponding may be preferable. After the 30-day curing period, the stabilized sludge is excavated from small holding ponds and trucked to the landfill. More exact control must be exercised in order to ensure that the sludge cures properly before excavation.

In cases where a temporary storage site is not available, direct landfilling can be accomplished immediately following the addition of dry fly ash, lime, and Calcilox to filtered sludge solids. Sludge treated in this manner can be efficiently transported to the landfill location, where only 5 to 6 days curing is needed before spreading.

Costs—

Limited operating experience with sludge fixation has similarly limited the disposal cost data base. Several major studies have involved detailed cost analyses of FGD sludge management alternatives. Table 3 displays selected cost estimates for the various processes described previously (ref. 7). In general, these figures show that the dry forms of fixation are typically only 10 to 20 percent more expensive than full dewatering and landfilling. This similarity is due to the common dewatering, transport, and handling requirements for each process. There is a greater differential in cost between wet disposal of untreated sludge and fixed sludge, due primarily to the lack of treatment, handling, and disposal requirements for the untreated material. As expected, the disposal of untreated (thickened only) FGD sludge is the most economical form of disposal, but may also be the most environmentally unacceptable (ref. 8). As the state-of-the-art in sludge fixation technology and full-service contractuals evolves, the cost differentials will become more distinct. The figures shown in Table 3 represent the cost ranking for disposal alternatives at a model power plant, and do not represent an absolute ranking for all situations.

The cost of other fixation methods not discussed here is typically higher, due in part to the use of additives that are less readily available. The selection of a fixation process therefore will be based upon the availability of ash or other dry waste material and the volume of waste to be treated, due to certain economies of scale.

DISPOSAL

Lagoon and landfill disposal of sludge are common and well documented elsewhere. Another disposal option that is less well known, and is therefore the focus of the following discussion, is land spreading. Land spread-

TABLE 3. COST ESTIMATES FOR SELECTED FGD SLUDGE DISPOSAL ALTERNATIVES

		Revenue requirements			
		$/Dry ton		$/Wet ton	
Process	Disposal option	Range	Base	Range	Base
Limestone Scrubbing	Dravo Fixation[¶]	20.41-10.87	15.32	10.21-5.44	7.66
	IUCS Fixation[#]	20.68-8.23	12.55	12.59-5.02	7.63
	Untreated[‖]	12.12-5.55	8.08	6.06-2.77	4.04
Lime Scrubbing	Dravo Fixation[¶]	17.77-9.47	13.34	8.89-4.74	6.67
	IUCS Fixation[#]	23.77-9.46	13.88	14.47-5.77	8.46
	Untreated[‖]	13.93-6.38	8.87	6.97-3.18	4.44

[¶] Base, Dravo

New 500-MW plant (30-yr life); midwest plant location; coal analysis (by wt): 3.5 percent sulfur (dry basis), 16 percent ash, Flyash removed with SO_2. Limestone process with 1.5 stoichiometry based on SO_2 removed. Pond characteristics: clay-lined, 1 mi from scrubber facilities, 50 percent solids settled density, 21.38 ft total depth, 414 acres. Calcilox added at 7 percent of dry solids.

[#] Base, IUCS

New 500-MW plant (30-yr life); midwest plant locations; coal analysis (by wt): 3.5 percent sulfur (dry basis), 16 percent ash. Flyash removed with SO_2. Limestone process with 1.5 stoichiometry based on SO_2 removed. Disposal in landfill 1 mi from scrubber facilities (by truck) 60 percent solids cakes. Lime added at 4 percent of dry solids.

[‖] Base, Untreated

New 500-MW plant (30-yr life); midwest plant location; coal analysis (by wt): 3.5 percent sulfur (dry basis), 16 percent ash. Flyash removed with SO_2. Limestone process with 1.5 stoichiometry based on SO_2 removed. Pond characteristics: clay-lined, 1 mi from scrubber facilities, 50 percent solids settled density, 21.21 ft total depth, 407 acres.

Source: Reference 7.

ing has the potential advantages of permitting utilization of the waste and minimizing the pretreatment required. The extent to which these potential advantages can be realized in the textile industry will depend in large part on future regulations being developed under RCRA.

Land spreading is a disposal technique by which organic wastewater or sludge is mixed with the surface soil to achieve volume reduction and degradation (ref. 9). This same disposal method is also referred to as land cultivation, land farming, sludge farming, soil incorporation, and other names. The practice involves several steps: (1) application of waste onto the surface soil; (2) mixing the waste with the soil to aerate the mass and expose the waste to soil microorganisms; (3) possibly adding nutrients or other soil amendments (i.e., limestone) during site preparation; and (4) remixing the soil/waste mass periodically to promote biodegradation. In practice, sludges are hauled to the disposal site either directly from the wastewater treatment plant or from an interim storage lagoon. The sludges are applied to the land by spraying, spreading, or subsurface injection. The field is then disced or plowed by conventional farm cultivation equipment.

Important processes that contribute to waste volume reduction include microbial degradation; microbiological degradation, including chemical and photochemical degradation; and evaporation and volatilization. There are ordinarily large numbers of diverse microorganisms in soils, consisting of several groups that are predominantly aerobic in well-drained soils. These microorganisms normally adhere to the surfaces of the soil colloids. The majority of groups are heterotrophic, deriving energy from the breakdown of organic substances, and these are the dominant microorganisms responsible for waste decomposition. The principal groups of organisms (in surface soils) include bacteria, actinomycetes, fungi, algae, and protozoa (ref. 10). The bacteria are the most numerous, the most biochemically active, and generally the most significant in terms of waste degradation.

The dependence of microorganism activity on environmental conditions such as soil pH, air temperature, soil water content, and nutrients has been well documented (refs. 11,12,13, 14). In general, pH between 5 and 8, warm air temperatures, moderately well-drained soils, and adequate nutrient availability favor soil microorganism activity and waste degradation. For any set of environmental conditions, however, waste degradation depends significantly on waste characteristics.

In recent years, considerable emphasis has been placed on the biodegradability of organic substances that are considered potential environmental toxins. Studies on the biodegradation of pesticides in soils illustrate the importance of waste characteristics. The chemical structure, nature, and position of substituting groups of the pesticides affect the extent and rate of microbial degradation, as demonstrated by the persistence of various pesticides in soils (ref. 11). Although some of the toxic organic substances do persist in soils, microbial degradation will eventually proceed if the substances are adsorbed in the soil surface for a sufficient period of time. There is, however, limited information on environmental factors affecting degradation of these substances as well as the microorganisms and enzymatic reactions involved.

Nonbiological degradation processes also play an important role in the dissipation of many organic substances in soils, including pesticides. In particular, considerable evidence has been reported on the importance of chemical hydrolysis and photochemical degradation (ref. 15). Other reactions, including oxidation-reduction, are important for certain compounds.

Chemical degradation of waste materials in soil is a widespread and complex phenomenon. Various mechanisms of chemical degradation or transformation have been found or postulated, including oxidation, reduction, hydrolysis, isomerization, and polymerization. The degradation rate depends on whether the reaction occurs in solution or on an absorbent surface, and is usually a function of pH; redox potential (Eh); surface acidity; and the nature, concentration, and availability of catalytic sites (ref. 9). Hydrolysis reactions are important steps in the degradation of many organic compounds, including chloro-triazine herbicides and organophosphate insecticides. These reactions are catalyzed by clay present in the soil (ref. 16).

Chemical reactions induced by electromagnetic radiation represent a potentially important pathway for alteration and/or degradation of many organic substances applied to soil. However, photochemical degradation should play a minor or negligible role in most land spreading applications since the waste is incorporated into the soil, thus reducing the amount of light received by the waste. Similarly, photochemical degradation assumes minor importance when mobile wastes are leached from the zone of photolytic influence.

Evaporation is a major mechanism of volume reduction. The rate of evaporation from a wet soil is controlled by the environmental conditions that control the rate of evaporation from bulk water and not by the properties of surface soil. However, frequent mixing of the waste with soil will increase evaporation loss and decrease the probability of developing anaerobic conditions.

The waste volatilization process is dependent on the vapor pressure of the compound and its rate of movement away from the evaporating surface. The magnitude of volatilization loss depends on the soil moisture content, chemical and physical properties of the waste and soil, atmospheric conditions (temperature, wind velocity, relative humidity, etc.), and application method (ref. 17). In land spreading, mixing the waste with soil should significantly reduce volatilization loss due to increased adsorption of the chemical by soil organic matter and clay, and the decreased vapor pressure of the waste material.

Municipal wastewater treatment sludges are widely applied to land for treatment and disposal, although new regulations may limit this practice for sludges which contain significant quantities of environmental toxins. Although to a lesser extent, land spreading is also used as a sluge disposal method in several industries, including food processing, wood preserving, pulp and paper, pharmaceuticals, soap and detergents, organic chemicals, petroleum refining, leather tanning, and textiles (ref. 18).

The extent to which the estimated 39,000 metric tons of sludge generated annually by the textile industry (1977) is amenable to land spreading disposal will depend on specific waste characteristics, applicable regulations to be promulgated under RCRA, and site-specific conditions. Thus, estimates of the quantity of textile sludge destined for land spreading disposal are not currently available.

Textile-Specific Considerations

To date, there has been limited experience with land spreading of textile sludge. The physical characteristics of textile industry sludge are reasonably similar to municipal sludge, so that equipment used for municipal sludge should be appropriate for textile sludge. However, other design and operational considerations such as waste loading rate, site selection, site management, and their associated environmental impacts may be significantly different than those associated with land spreading of municipal sludge due to different sludge characteristics. In addition, even sludges that appear to be similar based on analytical measurements may behave differently in response to land spreading if they have significantly different origins. Thus, additional investigation of textile sludge land spreading is required to determine the extent of its applicability.

Some limited work has been done on land spreading of sludge from textile and related industries which indicates that the subject is worth pursuing. For example, both preliminary greenhouse experiments and 3 years of full-scale field experience with land spreading of wastewater treatment sludge from an organic chemical plant which produces primarily dyes, dye intermediates and carriers, and pigments for use in the textile industry indicates that the practice has some beneficial and no apparent detrimental effects on turf grass production. It should be noted that the heavy metal content of the sludge is maintained at low levels (generally less than 5 ppm wet weight) through pretreatment of individual process waste streams before discharge to the treatment plant. Thus, future use of the disposal site for production of food chain crops should be unlimited (ref. 18).

In another instance, wastewater treatment sludge from an integrated denim mill is land spread on land used for sorghum and corn production. Detailed monitoring data from 2 years of full-scale field operation is scheduled for release in the spring. Preliminary results indicate that relatively low concentrations of heavy metals are present in the sludge and that plant uptake of heavy metals is at low enough levels to protect public health (ref. 19).

Costs

Costs, as well as technical feasibility, are always an important concern with any disposal method. Cost data on land spreading of textile sludge were not available for preparation of this paper. The unit costs for land spreading of sludge generated by five other industries are shown in Figure 1 (ref. 18). Also shown is the expected range of costs for a hypothetical commercial land cultivation site, estimated on the basis of a conceptual design. All of the unit costs presented include expenditures for land, equipment, labor, interim onsite storage of waste, and environmental monitoring. Costs for waste transport to the site are not included.

Capital costs for the conceptual design range from \$262,000 to \$746,000, for waste delivery rates from 1,000 to 4,000 dry metric tons (5,350 to 21,370 × 10^6 gal) per year of sludge at 5 percent solids. Costs for disposal of uncontained industrial wastes by sanitary landfill methods generally range from \$5.30 to \$22.00 per m^3 (\$0.02 to \$0.08 per gal), depending on location, site volume, and other factors. For industrial waste disposed in drums or other containers, costs can be substantially higher, ranging up to \$194 per m^3 (\$0.72 per gal). Thus, land cultivation cost is comparable with or lower than conventional disposal methods.

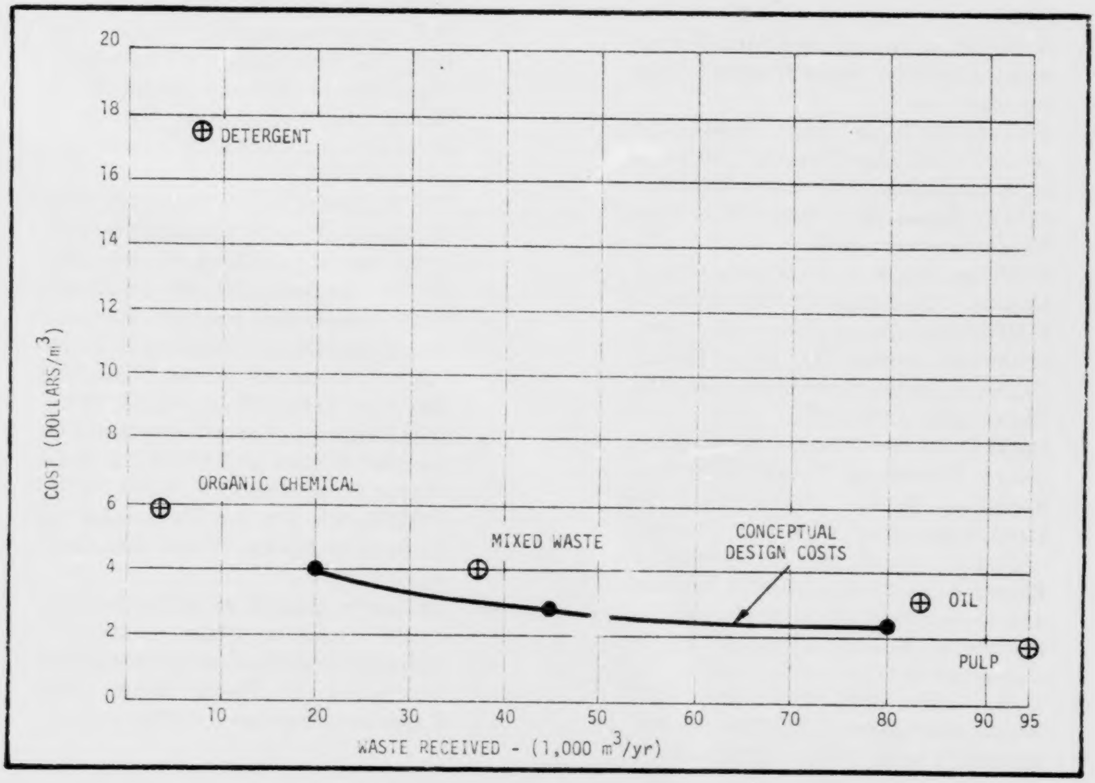


Figure 1. Land spreading costs.

REFERENCES

1. Versar, Inc., Assessment of Industrial Hazardous Waste Practices — Textiles Industry, U.S. Environmental Protection Agency Contract No. 68-01-3178, Springfield, VA, June 1976.
2. P. W. Powers, *How to Dispose of Toxic Substances and Industrial Wastes,* Noyes Data Corporation, Park Ridge, NJ, no date.
3. E. C. Lazar, "Summary of Damage Incidents From Improper Land Disposal," Proceedings of the National Conference on Management and Disposal of Residues From the Treatment of Industrial Wastewaters, Washington, DC, pp. 253-257, February 1975.
4. M. P. Lehman, "Industrial Waste Disposal Overview," Proceedings of the National Conference on Management and Disposal of Residue From the Treatment of Industrial Wastewaters, Washington, DC, pp. 7-12, February 1975.
5. B. Paulsrud, unpublished data, Norwegian Institute for Water Research, Oslo, Norway.
6. Michael Baker, Jr., Inc., "State-of-the-Art of FGD Sludge Fixation," prepared for Electric Power Research Institute, FP-671, Research Project 786-1, Final Report, January 1978.
7. J. W. Barrier, H. J. Faucett, and L. J. Henson, "Comparative Economics of FGD Sludge Disposal," for presentation at the 71st Annual Meeting of the Air Pollution Control Association, Houston, Texas, June 25-30, 1978.
8. Dallas E. Weaver, Curtis J. Schmidt, and John P. Woodyard, "Data Base for Standards/Regulations Development for Land Disposal of Flue Gas Cleaning Sludges," Municipal Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, EPA-600/7-77-118, December 1977.
9. C. R. Phillips and J. Nathwani, "Soil-Waste Interaction: A State-of-the-Art Review," Solid Waste Management Report EPS 3-EC-76-14, Environment Canada, October 1976.
10. F. E. Broadbent, "Organics," Proceedings of the Joint Conference on Recycling Municipal Sludges and Effluents on Land, Champaign, Illinois, pp. 97-101, July 9-13, 1973.
11. M. Alexander, *Introduction to Soil Microbiology,* John Wiley and Sons, New York, NY, 1961.
12. M. Alexander, "Biodegradation: Problems of Molecularrecalcitrance and Microbial Fallibility," *Adv. Applied Microbiol.*, Vol. 7, pp. 35-80, 1965.
13. J. P. Martin and D. D. Focht, "Biological Properties of Soils," *Soils for Management of Organic Wastes and Waste Waters,* American Society of Agronomy, Madison, Wisconsin, pp. 115-169, 1977.
14. R. H. Miller, "The Soil as a Biological Filter," *Proceedings on Conference on Recycling Treated Municipal Wastewater through Forest and Cropland,* EPA 660/2-74003, U.S. Environmental Protection Agency, 1974.
15. D. E. Armstrong and J. G. Konrad, "Nonbiological Degradation of Pesticides," *Pesticides in Soil and Water,* W. D. Guzeni, ed., Soil Science Society of America, Inc., Madison, Wisconsin, pp. 123-131, 1974.
16. J. G. Konrad et al., "Soil Degradation of Diazinon, a Phosphorothioate Insecticide," *Agron,* Vol. 59, pp. 591-594, 1967.
17. W. F. Spencer and M. J. Cliath, "Vaporization of Chemicals," Environmental Dynamics of Pesticides, R. Haque and V. H. Freed, eds., Plenum Publishing Co., New York, NY, pp. 61-78, 1975.
18. SCS Engineers, "Land Cultivation of Industrial Wastes and Municipal Solid Waste: State-of-the-Art Study," EPA-600/2-78-140a & b, U.S. Environmental Protection Agency, Cincinnati, Ohio, April 1978.
19. Dr. Larry King, Dept. of Soil Science, North Carolina State University, Raleigh, North Carolina, personal communication to David Bauer, SCS Engineers, October 5, 1978.

Session V: ASSESSMENT METHODOLOGY

Dale A. Denny, Session Chairman

LEVEL 1 MEASUREMENT PROCEDURES FOR EFFLUENT CHARACTERIZATION

R. G. Merrill, Jr., L. D. Johnson, J. A. Dorsey*

Abstract

The EPA/IERL-RTP phased approach and its applications to environmental assessment of textile wastewaters are discussed in this presentation. In the first phase, Level 1, methods have been developed and applied to a variety of industrial and energy sources. The procedures are multimedia and accordingly have application to liquid effluent streams as well as air and solid waste streams. The Level 1 procedures have been applied to the effluent streams from 15 textile plants. The results of the chemical and biological analyses are discussed in light of their successful use in ranking the plants for further biological and chemical analysis and for evaluation of best available control technology (BAT). The use of selected Level 1 biological tests for control technology evaluation is also outlined.

INTRODUCTION

New Environmental Protection Agency (EPA) regulations and guidelines, as mandated by Congress and the Clean Air Act, place increasingly greater demands on EPA's research programs. Not only are EPA's research laboratories given the mission of evaluating pollution control devices, but they must also develop effective methods of providing the Agency and the public with a thorough understanding of the nature and magnitude of current and future environmental assessment problems. The comprehensive assessment of environmental insult posed by stationary sources is one of the major missions of the Industrial Environmental Research Laboratory (IERL) at Research Triangle Park, NC. An outgrowth of this mission is the IERL-RTP Environmental Assessment Program.

The Environmental Assessment (EA) Program is designed to pursue four major goals in the environmental assessment of a stationary source. They are:

1. A systematic evaluation of the physical, chemical, and biological characteristics of all streams associated with a process.
2. Predictions of the probable effects of those streams on the environment.
3. Prioritization of those streams relative to their individual hazard potential.
4. Identification of any necessary pollution control technology programs.

Outputs of the EA program are primarily intended to define the need for and design of control technology, and to provide a data base sufficient to meet the planning needs of the regulatory and standard-setting parts of the Agency.

In order to focus available resources (both manpower and dollars) on emissions and fulfill the goals of the EA program, a 3-phased approach was developed after consideration of and comparison to more traditional approaches (refs. 1,2).

The phased approach (refs. 3,4,5,6,7) utilizes three closely linked levels of sampling and analysis. Level 1 is a screening or survey phase, Level 2 is directed toward confirmation of Level 1 information based on more detailed analysis, and Level 3 involves monitoring of selected pollutants determined by the results of Levels 1 and 2. Level 3 may also include the study of chronic sublethal effects constituting partial or complete assessment of risk.

Each level includes consideration of the commensurate sampling, chemical, and biological methods in order to meet the goals of the assessment. Level 1 methods have been developed and applied to a variety of industrial and energy sources including textile wastewaters. This experience with Level 1 procedures has provided firsthand knowledge of the limitations of the techniques and aided early revision of areas found to be deficient. The Level 2 sampling and chemical analysis approach is

---

*U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, NC.

Preceding page blank

nearly complete in a broad conceptual sense. Close monitoring of field and laboratory implementation is now required to verify that Level 2 meets the required goals.

The conceptual approach to Level 2 biological testing is well underway and planning for Level 3 approaches to sampling and chemical analysis is also currently underway.

LEVEL 1 OVERVIEW

The multimedia Level 1 sampling, sample preparation, and analytical procedures (shown in Figure 1) have been developed to address liquid, gaseous, and solid waste streams (refs. 8,9,10). Briefly, the procedures provide screening results within broad general limits for the chemical composition and rate of emission of inorganic species (as elements) and organic species (as compound classes). The Level 1 procedures also provide an indication of direct biological response in the health, aquatic ecological, and terrestrial ecological areas. The overall goal for accuracy at Level 1 is to report the results within a factor of 3. In simple terms, this means that a reported value between 30 and 300 is acceptable when the true measurement is 100. The methods currently in use are capable of much greater accuracy and precision individually, but the overall relaxation of

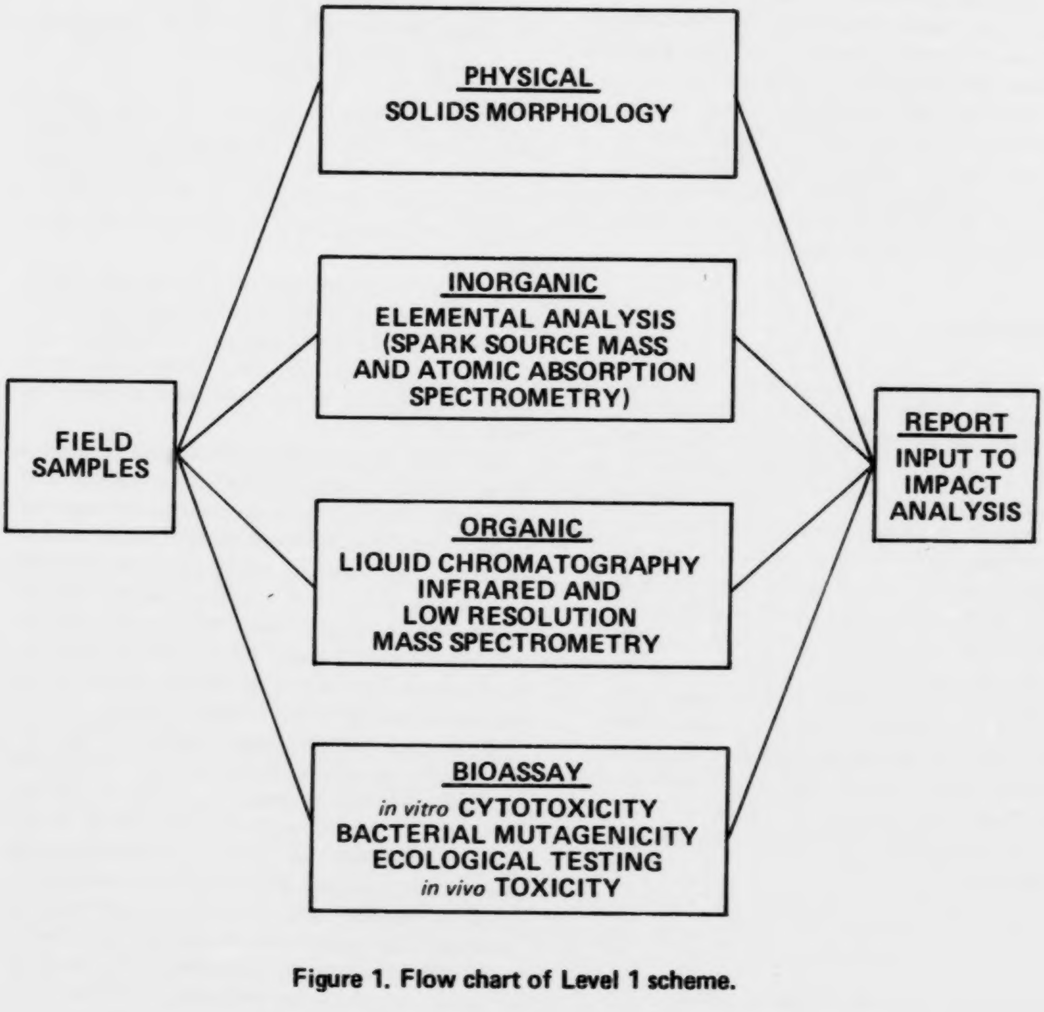

PHYSICAL
SOLIDS MORPHOLOGY
INORGANIC
ELEMENTAL ANALYSIS (SPARK SOURCE MASS AND ATOMIC ABSORPTION SPECTROMETRY)
FIELD SAMPLES
REPORT
INPUT TO IMPACT ANALYSIS
ORGANIC
LIQUID CHROMATOGRAPHY INFRARED AND LOW RESOLUTION MASS SPECTROMETRY
BIOASSAY
in vitro CYTOTOXICITY
BACTERIAL MUTAGENICITY
ECOLOGICAL TESTING
in vivo TOXICITY

Figure 1. Flow chart of Level 1 scheme.

traditional analytical limits allows a significant cost savings. These savings are typified by the use of grab sampling instead of integrated sampling, where possible, and by the use of gravimetric results, where they are applicable, rather than the use of higher priced analytical techniques. When necessary, more costly sampling or analytical methods are used (ref. 9) as in the case of sampling particulate-laden stack gas streams in order to collect representative samples.

For aqueous fugitive effluents such as water and leachate runoff, samples may be acquired by means of simple plug collectors; however, the sampling plan may be complex and may involve careful consideration of procedures for the interpretation of the results.

Liquids and slurries contained in ditches, pipes, or holding areas (such as textile wastewaters) are sampled by the dipper or bucket grab procedure. If mechanical sampling devices are in place and available, these may be used to obtain Level 1 samples; however, they are not specified for Level 1 screening procedures. In fact, the Level 1 procedures leave considerable flexibility in sample acquisition design in order to allow grab or integrated sampling to be tailored to the source (ref. 8). For a reasonably consistent source, such as a holding pond effluent, a single point grab sample is usually acceptable. However, if serious changes occur or are suspected in the process stream over a period of time, then a 24-h composite should be collected from hourly subsamples.

Samples for laboratory chemical analysis are preserved by standard techniques; for biological testing they are shipped in ice without preservation. Additional details on sample acquisition and sample size requirements are given in the appropriate reference documents (refs. 8,9,10,11,12).

LEVEL 1 ANALYSIS METHODS APPLIED TO TEXTILE WASTEWATERS

An overview of sample handling for organic, inorganic, and biological analyses of aqueous samples is shown in Figure 2. Field procedures are indicated by solid lines and laboratory analyses by broken lines. Field analyses such as dissolved oxygen and pH are performed electrochemically with the appropriate electrode and are run on the neat unfiltered sample. Extraction for organic analysis is accomplished in the field at acidic and basic pH's. Filtration for total suspended solids is also done in the field and in accordance with standard EPA methods.

Tests performed in the laboratory for inorganic solids, filtrate, organic, and biological analyses are shown in Figures 3, 4, 5, and 6, respectively. Most of the inorganic analysis methods may be readily arranged into three major categories: spark source mass spectrometry, atomic absorption spectrometry, and standard water tests.

Spark source mass spectrometry is an exceptionally powerful survey tool, which yields results for approximately 70 elements with one analysis. This multielement capability gives the technique overwhelming cost or information advantages over competing techniques of atomic absorption, neutron activation, optical spectroscopy, and inductively coupled argon plasma emission spectroscopy. The primary disadvantage is lower accuracy; however, the results usually fall within the requirements for Level 1. Special problems with arsenic, antimony, and mercury analysis require application of atomic absorption techniques. The standard water tests are applied by use of a field test kit. These kits have accuracy sufficient for Level 1, and represent time and cost savings, as well as the option of field or laboratory application. These kits, as well as the standard methods from which they are derived, are widely known and will not be discussed in detail (refs. 13,14).

The one test that does not fit into the three categories for inorganic analysis is the leachable anions test. This test is only performed if impounding of the removed solids is evident or likely. Storage of large quantities of the solid materials could lead to drainage or runoff problems if toxic leachables are present. The current Level 1 specification for this test calls for test kit anion analysis of a distilled water leachate and an HCl leachate. New leachate procedures are being specified by the Hazardous Waste Management Division of EPA's Office of Solid Waste Management Programs. These procedures are under review by IERL-RTP, and will be adopted for Level 1 use if appropriate. The use of ion chromatography for analysis of leachable anions is also under

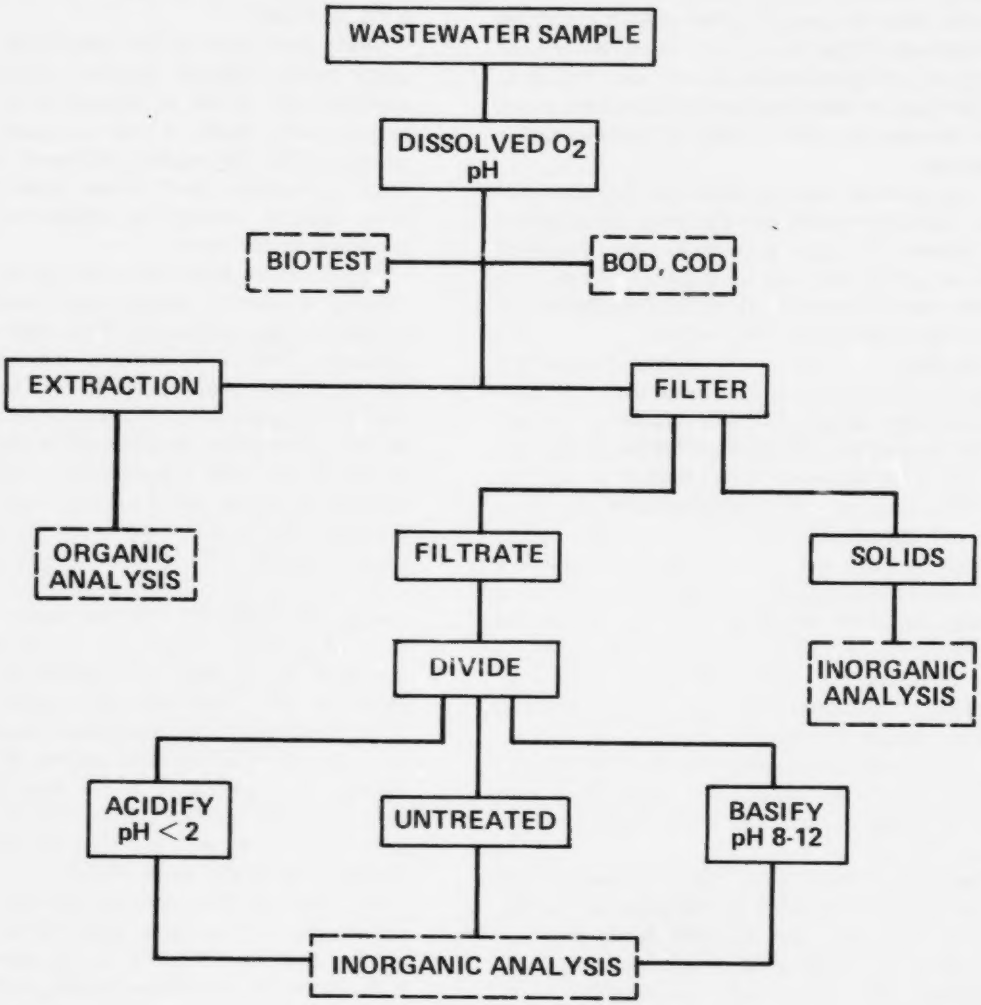

WASTEWATER SAMPLE
DISSOLVED O2
pH
BIOTEST
BOD, COD
EXTRACTION
FILTER
ORGANIC ANALYSIS
FILTRATE
SOLIDS
DIVIDE
INORGANIC ANALYSIS
ACIDIFY
pH < 2
UNTREATED
BASIFY
pH 8-12
INORGANIC ANALYSIS

Figure 2. Sample handling summary.

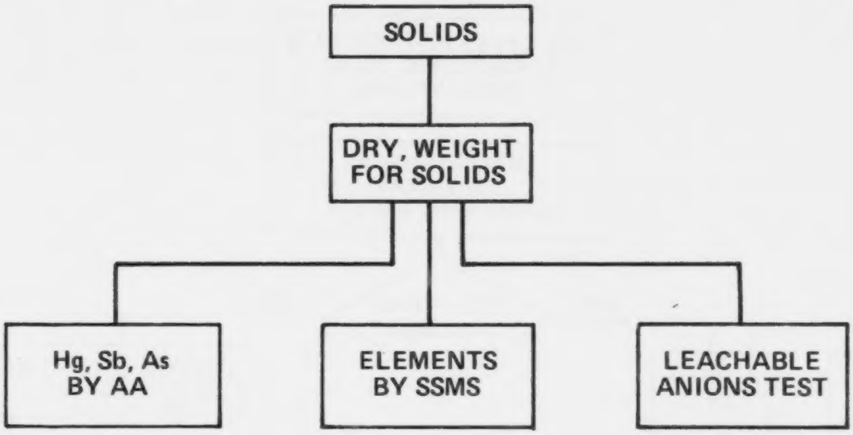

SOLIDS
DRY, WEIGHT FOR SOLIDS
Hg, Sb, As BY AA
ELEMENTS BY SSMS
LEACHABLE ANIONS TEST

Figure 3. Inorganic analysis of solids.

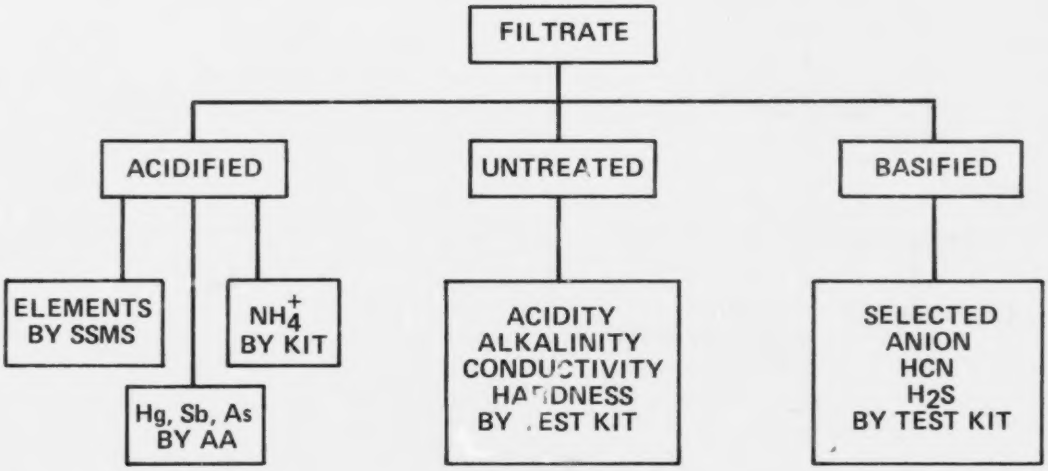

FILTRATE
ACIDIFIED
UNTREATED
BASIFIED
ELEMENTS BY SSMS
NH_4^+ BY KIT
Hg, Sb, As BY AA
ACIDITY
ALKALINITY
CONDUCTIVITY
HARDNESS
BY TEST KIT
SELECTED
ANION
HCN
H_2S
BY TEST KIT

Figure 4. Inorganic analysis of filtrate.

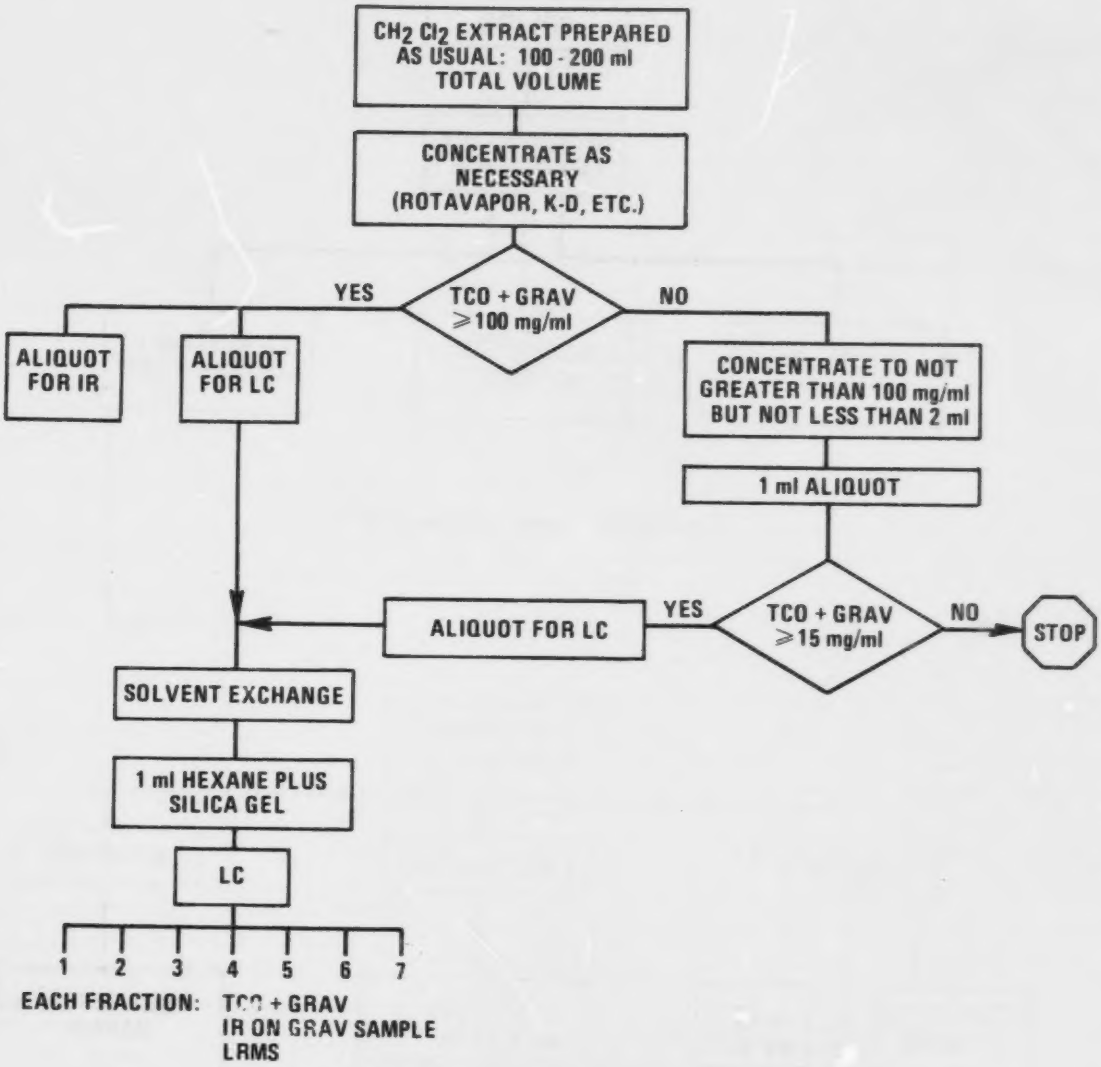

CH2 Cl2 EXTRACT PREPARED AS USUAL: 100 - 200 ml TOTAL VOLUME
CONCENTRATE AS NECESSARY (ROTAVAPOR, K-D, ETC.)
TCO + GRAV ≥100 mg/ml
YES
NO
ALIQUOT FOR IR
ALIQUOT FOR LC
CONCENTRATE TO NOT GREATER THAN 100 mg/ml BUT NOT LESS THAN 2 ml
1 ml ALIQUOT
TCO + GRAV ≥15 mg/ml
YES
NO
STOP
ALIQUOT FOR LC
SOLVENT EXCHANGE
1 ml HEXANE PLUS SILICA GEL
LC
1
2
3
4
5
6
7
EACH FRACTION: TCO + GRAV
IR ON GRAV SAMPLE
LRMS

Figure 5. Modified Level 1 organic analysis procedure.

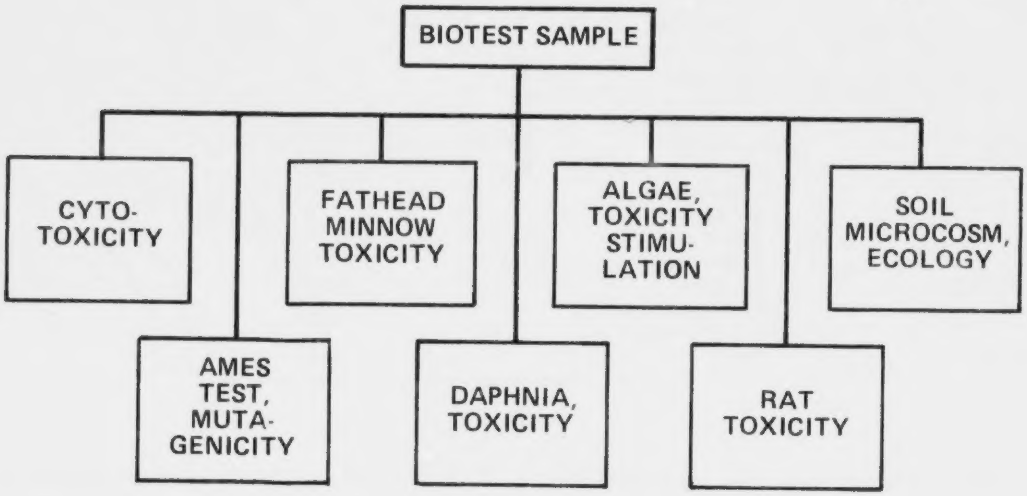


Figure 6. Biotest analysis.

review and will be adopted where applicable for use in Level 1.

The organic analysis scheme requires more description for understanding of its nature. Specific compound identification should not, in general, be expected at costs commensurate with the Level 1 philosophy. Therefore, the scheme presented is relatively simple and inexpensive, yet it produces information that can be utilized to decide whether more sophisticated and expensive methods are justified. The Level 1 organic analysis produces data on chromatographic classes of compounds, characteristics of infrared absorption bands, and further class information from low resolution mass spectrometry (LRMS).

The Level 1 organic analysis strategy contains four analytical operations that are central to the scheme: liquid chromatographic separation, total organics content determination, infrared absorption spectrophotometry, and LRMS.

The first organic analysis operation is the determination of total organics content. This operation allows initial quantitation of the organics in the unfractionated sample for aliquot size selection for optimum column operation and subsequent quantitation of material from each chromatographic fraction. The original Level 1 scheme (ref. 1), as well as the first revision, depended entirely upon reduction to dryness and weighing for total organics determination. More recent data show that many materials in the boiling range below 275° C may be partially lost by that approach (ref. 15). Accordingly, a gas chromatography procedure for volatile organics has been adopted as a part of the Level 1 strategy (ref. 5). Total organic content is obtained by addition of the gravimetric results and the total chromatographable organics (TCO).

Liquid chromatographic separation, the second organic analysis operation, is the heart of the whole approach. It is an analytical step (in that behavior of a given class of compounds is predictable) as well as a separation step (since the fractions may be further analyzed much more readily than the original mixture). Distribution of a few selected compounds is shown in Table 1.

The third organic analysis operation is infrared absorption spectrophotometry. This classical technique is often overlooked in today's mass-spectrometry-dominated laboratory, but still remains a powerful tool providing considerable information at a moderate cost. Infrared spectra of the seven chromatographic fractions may be used to confirm the absence or presence of particular compound classes or functional groups as indicated by the chromatographic data. It is occasionally possible to obtain specific compound identification

TABLE 1. PERCENT DISTRIBUTION IN LC FRACTIONS (FROM REFERENCE 9)

Compound	1	2	3	4	5	6	7
Hexadecane	85	15					
Cumene		82	17				
Dichlorobiphenyl	25	69	5				
Acenapthene		69	31				
Tetrachloroethane		81	19				
o-Nitrotoluene			30	70			
Benzaldehyde			22	75	3		
Dihexyl ether			18	77	4		
N-methyl aniline					3	94	2
Quinoline						100	
Diethyl phthalate						100	
2-ethyl hexanol						99	0.7
Phenol						100	

from the infrared spectra. But, as previously mentioned, the complexity of most environmental samples makes this the exception rather than the rule.

The fourth organic analytical operation of the Level 1 organic scheme is LRMS. The original Level 1 scheme did not contain LRMS (ref. 10), but it was included in the modified strategy (ref. 8) to prevent potential triggering of Level 2 efforts based on large amounts of suspicious, but innocuous, organics. LRMS can be a very powerful tool, especially when combined with the other Level 1 components. In many cases, compound identification and quantification are possible when the entire scheme is applied.

There are advantages to employing LRMS rather than the more powerful high resolution mass spectrometry (HRMS) or the more popular gas chromatography/mass spectrometry (GCMS). HRMS is roughly 4 times as expensive as LRMS. The detailed information and compound specificity available from this technique are far beyond the original goal of Level 1, and HRMS is not readily available for the quantity of samples envisioned. GCMS is also more expensive than LRMS and it has the added disadvantage of detecting only chromatographable materials. Both HRMS and GCMS are considered excellent Level 2 techniques.

The Level 1 biological tests (ref. 12) typically applied to aqueous samples, such as textile wastewaters, are shown in Figure 6. In vitro analysis for mutagenicity is performed using four *salmonella typhimurium* strains in the Ames assay. Cellular toxicity of aqueous effluents is assayed using WI-38 human lung fibroblasts. Acute in vivo testing in rodents is performed as a quantal (all or none) assay. If gross toxic responses occur, a second quantitative assay is performed. The aquatic ecological effects tests include a vertebrate (fish), an invertebrate (daphnia or shrimp), and an algae of either fresh or marine origin depending on the impact of the effluent to fresh or marine environments. The terrestrial ecological effects tests include assays with higher plants and intact soil cores.

The results of the biological tests at Level 1 not only provide a measure of direct biological response in health, aquatic ecological, and terrestrial ecological areas, but also aid in overall ranking of the streams from one or a series of stationary sources.

RESULTS OF LEVEL 1 SAMPLING AND ANALYSIS

A few summary examples of the data and their use are given in Tables 2 and 3. These tables reflect the manner in which the chemical data can be used to rank 15 textile effluents using either a human health model or an aquatic ecological model. Table 4 details the outcome of using only Level 1 biological results to rank the same streams. Together, the chemical and biological rankings provide complementary information leading to a minimun possibility of

TABLE 2. HEALTH EFFECTS: SUMMARY OF CHEMICAL AND BIOLOGICAL TEST RESULTS OF TEXTILE EFFLUENTS

Plant	1a DOH	1b DOH	2 AMES	3 RAM	4 WI-38	5 RAT
U	8.86×10^2	2.9474	N	N	*	N
S	8.35×10^2	2.9217	N	*	*	N
L	8.36×10^3	3.9224	N	M	L	N
W	4.99×10^3	3.6984	N	L	*	N
T	3.35×10^3	3.5245	N	M	*	N
N	3.28×10^3	3.5161	N	M	L	N
V	5.19×10^2	2.7152	N	N	*	N
F	4.52×10^2	2.6551	N	L	*	N
B	3.30×10^2	2.5185	N	N	*	N
K	1.43×10^2	2.1553	N	N	*	N
A	1.14×10^2	2.0569	N	N	*	N
C	9.90×10^1	1.9956	N	L	*	N
G	9.40×10^1	1.9731	N	N	*	N
X	3.60×10^1	1.5563	N	L	*	N
E	3.30×10^1	1.5185	N	N	*	N

* = data not available
M = moderate toxicity rating
L = low toxicity rating
N = no detectable toxicity
1a = DOH = degree of hazard
1b = DOH = degree of hazard ($\log_{10}$)
2 = AMES = mutagenicity test
3 = RAM = rabbit alveolar macrophage
4 = WI-38 = human embryonic lung cells
5 = RAT = rodent acute toxicity

underestimating a potential environmental insult.

RELEVANT ONGOING STUDIES

Although considerable effort has gone into development of the phased approach to environmental assessment, there are still many areas requiring further investigation and improvement. The results of data gathered during the application of the phased approach to environmental assessments have provided guidance to IERL-RTP in planning supportive investigations for Levels 1, 2, and 3. Listed below are relevant studies that have resulted from the experience gained from assessments conducted to date.

- Use of porous polymer resins for sampling of organics from water.
- Sampling and analysis of highly water-soluble organics.
- Interpretation and synthesis of Level 1 chemical, biological, and engineering data.
- Increased accuracy of spark source mass spectrometry (SSMS) analysis, and extension to arsenic and antimony.
- Use of ion chromatography for anion analysis.
- Evaluation and upgrading of the terrestrial biological tests.

The objective of Level 1 sampling and analysis is to provide cost-effective screening information for source assessment. This objective requires a comprehensive approach rather than a specific one. Specificity is left for Level 2.

Evaluation of control technology for its effectiveness and ability to perform over typical variations in stream composition is an integral part of Level 3. The use of selected Level 1 analyses specifically from the biological testing scheme is a distinct possibility at Level 3. This

TABLE 3. ECOLOGICAL EFFECTS: SUMMARY OF CHEMICAL AND BIOLOGICAL TEST RESULTS OF TEXTILE EFFLUENTS

Plant	6a DOH	6b DOH	7 FW ALGAL	8 FW FISH	9 FW DAPHNIA	10 SW ALGAL	11 SW FISH	12 SW GRASS SHRIMP
N	1.51×10^5	5.1806	M	L	H	M	L	L
L	6.07×10^4	4.7830	N	L	L	M	N	N
C	3.62×10^4	4.5589	N	L	L	L	L	L
B	3.05×10^4	4.4836	L	N	N	N	N	N
E	2.91×10^4	4.4638	M	N	M	L	N	N
V	2.54×10^4	4.4051	N	L	M	L	*	*
F	2.23×10^4	4.3482	N	N	L	L	N	N
T	1.56×10^4	4.1939	N	L	N	L	L	L
U	1.46×10^4	4.1646	N	N	L	N	N	N
A	1.36×10^4	4.1345	N	L	M	*	L	L
G	1.15×10^4	4.0618	N	L	L	L	N	N
K	1.06×10^4	4.0249	N	N	N	L	N	N
S	9.48×10^3	3.9770	N	N	*	N	N	N
W	5.62×10^3	3.7494	N	L	M	L	L	L
X	3.43×10^2	2.5353	N	N	N	N	N	N

* = data not available
H = high toxicity rating
M = moderate toxicity rating
L = low toxicity rating
N = no detectable toxicity

6a = DOH = degree of hazard
6b = DOH = degree of hazard ($\log_{10}$)
7 = FW ALGAL = freshwater algal
8 = FW FISH = fathead minnow
9 = FW DAPHNIA = freshwater invertebrate
10 = SW ALGAL = marine algal
11 = SW FISH = marine sheepshead minnow
12 = SW GRASS SHRIMP = saltwater shrimp

TABLE 4. PRIORITIZATION OF TEXTILE PLANTS BY TOXICITY OF SECONDARY EFFLUENT

Toxicity ranking	Plant
Most toxic	N, A
	W
	C, T
	V, L
Least Toxic	S
Nontoxic	B, E, F, G, K, U, X

approach has been employed to determine the reduction in toxicity before and after tertiary treatment at plants selected as high priority from the 15 sites screened by Level 1.

Many methods and their uses have been touched upon in a fairly cursory manner in an attempt to present an overview in a reasonable amount of time and space. More details can be found in the references cited.

REFERENCES

1. J. W. Hammersma and S. L. Reynolds, "Field Test Sampling/Analytical Strategies and Implementation Cost Estimates: Coal Gasification and Flue Gas Desulfurization," EPA-600/2-76-093b, NTIS No. PB 254166, April 1976.
2. J. Vlahakis and H. Abelson, "Environmental Assessment Sampling and Analytical Strategy Program," EPA-600/2-76-093a, NTIS No. PB 261259, May 1976.
3. L. D. Johnson, "Proceedings for Environ-

mental Assessment of Industrial Wastewater," *Symposium Proceedings: Third Annual Conference on Treatment and Disposal of Industrial Wastewaters and Residues,* Houston, TX, April 1978.

4. J. A. Dorsey, L. D. Johnson, R. M. Statnick, and C. H. Lochmuller, "Environmental Assessment Sampling and Analysis: Phased Approach and Techniques for Level 1," EPA-600/2-77-115, NTIS No. PB 268563, June 1977.
5. L. D. Johnson and R. G. Merrill, "Organic Analysis for Environmental Assessment," *Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, III* (September 1977, Hollywood, FL), EPA-600/7-78-063, NTIS No. PB 282429, April 1978.
6. R. M. Statnick and L. D. Johnson, "Measurements Programs for Environmental Assessment," *Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, II* (December 1975, Hollywood, FL), EPA-600/2-76-149, NTIS No. PB 257182, June 1976.
7. L. D. Johnson and J. A. Dorsey, "Environmental Protection Agency Level 1 Chemistry: Status and Experiences," Symposium Proceedings: *Symposium on Potential Health and Environmental Effects of Synthetic Fossil Fuel Technologies,* Gatlinburg, TN, September 1978.
8. J. W. Hammersma, S. L. Reynolds, and R. F. Maddalone, "IERL-RTP Procedures Manual: Level 1 Environmental Assessment," EPA-600/2-76-160a, (NTIS No. PB 257850, June 1976.
9. D. B. Harris, W. B. Kuykendal, and L. D. Johnson, "Development of a Source Assessment Sampling System," presented at the Fourth National Conference on Energy and the Environment, Cincinnati, OH, October 1976.
10. P. W. Jones, A. P. Graffeo, R. Detrick, P. A. Clarke, and R. J. Jakobsen, *Technical Manual for Analysis of Organic Materials in Process Streams,* EPA-600/2-76-072, NTIS No. PB 259299, March 1976.
11. G. T. Brookman, J. J. Binder, and W. A. Wade, "Sampling and Modeling of Non-Point Sources at a Coal Fired Utility," EPA-600/2-77-199, NTIS No. PB 274369, September 1977.
12. K. M. Duke, M. E. Davis, and A. J. Dennis, *IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests for Pilot Studies,* EPA-600/7-77-043, NTIS No. PB 268484, April 1977.
13. American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* 14th Edition, APHA, Washington, DC, 1975.
14. U.S. Environmental Protection Agency, *Manual of Methods for Chemical Analysis of Water and Wastes,* EPA-625/6-74-003, 1974.
15. Arthur D. Little, Inc., Monthly Progress Report on EPA Contract 68-02-2150, April 1977, to be published in a forthcoming EPA report.

SHORT-TERM BIOTESTING OF ENVIRONMENTAL EFFLUENTS

Shahbeg S. Sandhu*

Abstract

The U.S. Environmental Protection Agency has proposed a phased approach for evaluating the health and ecological impact of industrial effluents. Biotesting is considered an integral part of this approach. The bioassays included in the first phase, Level 1, are relatively simple, inexpensive, and rapid. The data generated by these bioassays are considered to be of preliminary nature and are used only for prioritizing waste streams for further attention regarding implementation of control technology. Included in Level 1 are bioassays for the evaluation of effects on health, terrestrial ecology, freshwater ecology, and marine ecology. With the exception of one bioassay (Ames test), the tests included in Level 1 provide only the acute toxic effects. More extensive testing is required to verify the results obtained from the Level 1 test matrix.

INTRODUCTION

Environmental pollution created by the industrial nations has significantly increased during the last three decades. The revolution in the chemical industry after World War II and the increased demand for chemical products and byproducts have been responsible for increasing the quantities and distribution of hazardous substances in the biosphere. The need for developing new sources of energy involving synthetic fuels and coal conversion technologies has added new dimensions to the existing environmental problems.

Recent episodes arising from the lack of installing proper process control technology as in the case of Seveso in Italy, and mishandling of industrial waste as in the cases of the Love Canal in the United States and B. T. Kemi in Sweden have aroused public awareness to the hazards associated with industrial effluents and wastes.

Environmental assessment is an attempt to evaluate the overall health and ecological impact of industrial emissions, effluents, and wastes. The approach to environmental assessment is complicated by the awesome number of technologies that must be evaluated. It is not practical to provide a toxicological and ecological assessment of the emissions and effluents from these industrial sources by conventional means. Therefore, the development of inexpensive, short-term, and simple bioassays is a critical step in evaluating the health and ecological hazard from industrial technologies.

It is clear that chemical and biological analyses have a dual role in the process of environmental assessment. Chemical analysis, while indicative, cannot provide sufficient data for complete evaluation of potential pollutant effects because the biological activity of complex samples cannot be consistently predicted. Although bioassays can indicate the biological activity of a given sample, they cannot specify which components of a crude sample are responsible for the observed toxicity.

In considering the application of analytical chemical methodology, it is important to realize that the presence or absence of a known toxic component within a complex sample neither indicates nor precludes a relationship between that component and the biological activity of the sample. To avoid the possibility of overlooking unanticipated biologically active components, chemical analysis should not be restricted to determination of preselected known toxic compounds or suspected hazardous components of a complex sample. However, it may be technically overwhelming to analyze for all of the known or suspected hazardous components in a large number of complex samples. For this reason, and for cost effectiveness, it can be argued that a phased approach involving stepwise application of biological and chemical methodology is appropriate in evaluating the potential health and ecological hazard of complex mixtures.

The Industrial Environmental Research Laboratory of the Environmental Protection Agency, Research Triangle Park, NC (IERL-RTP), has delineated a 3-phase approach for

---

*Health Effects Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Preceding page blank

performing an environmental source assessment in order to determine the need for control technology (refs. 1,2). The scheme, shown in Table 1, involves the evaluation of process streams beginning with the least expensive and most rapid assays, mostly qualitative in nature, followed by more expensive and time-consuming assays mostly quantitative in nature. This approach provides an integrated application of physical, chemical, and biological tests at each level.

The first level (Level 1) involves rapid screening of a large number of industrial waste materials for their toxic and mutagenic effects. These results are used to prioritize streams for further evaluation in Level 2. In Level 2, the results obtained in Level 1 are validated and confirmed through more stringent and comprehensive toxicological techniques and the chemical and/or physical properties of the waste materials are determined in greater detail. Level 3 source assessment examines the composition and long-term variations of the more toxic waste streams and focuses on the long-term effects of these waste streams on biological systems.

The Level 1 bioassays include health and ecology related bioassays that, with the exception of one biotest, measure acute toxic effects. The matrix of Level 1 bioassays is shown in Table 2.

Because of the diverse physical forms of the industrial discharges (i.e., liquid, solid, and gaseous), all the Level 1 bioassays listed in Table 2 may not be applicable to all the samples. A suggested minimal test matrix is shown in Table 3. This matrix represents a minimum test battery required to indicate potentially adverse health and and ecological effects caused by an industrial waste stream.

DATA MANAGEMENT

The number and diversity of proposed bioassays employed in environmental assessment require the development of a uniform data reporting format that permits the examination, interpretation, and correlation of the results. The data from each bioassay are arbitrarily reduced to levels of toxicity—high, moderate, weak, or nondetectable.

The criteria for determining the level of toxicity (also shown in Table 4) are listed below.

Nondetectable—no significant response as determined by a preestablished set of criteria including statistical analysis where appropriate. The nondetectable classification would take into account certain toxicants that could be present in a sample below the level of detectability for the assay. This classification would also take into consideration methods for concentration and/or extraction.

Low—a significant response or LD_{50} (EC_{50}) ranging from the maximum dose applicable to the assay system (defined as MAD and established in advance) to one-tenth of that value. For example, if it is established that 10 g/kg will define the upper limit of sample application to rats in the acute rodent toxicity test, then any sample with an LD_{50} value ≤ 10 g/kg down to a concentration of 1 g/kg

TABLE 1. THE IERL-RTP PHASED APPROACH TO ENVIRONMENTAL ASSESSMENT

Level	Objective	Bioassays	Use
I.	Screening, detection	Simple, inexpensive, rapid Mostly qualitative data	Prioritization for further testing
II.	Verification, identification of toxic components	Mostly quantitative data, well-defined end points Expensive and comprehensive	Development of control technology
III.	Long-term effects	Animal and ecosystem studies, chronic exposure	Health and ecological hazard assessment

TABLE 2. IERL-RTP LEVEL 1 BIOASSAYS

Test system	Study time (weeks)	Sample	Approximate cost ($)
Health-related in vitro tests			
Ames salmonella/microsome mutagenicity	3	1 g/50 ml	600
RAM-cytotoxicity	3	0.5 g/50 ml	600
WI-38-cytotoxicity	3	0.5 g/50 ml	340
CHO-cytotoxicity	3	0 g/50 ml	340
Health-related in vivo tests			
Rodent range-finding test	4	100 g/liter	640
Freshwater toxicity ecology tests			
Algal	3	200 liters	1,570
Daphnia-static	1	200 liters	1,000
Fish	1	200 liters	1,570
Marine ecology tests			
Algal	3	50 liters	1,570
Fish		50 liters	
Shrimp	2		
Terrestial ecology related bioassays			
(Under development)			

TABLE 3. LEVEL 1 MINIMAL TEST MATRIX

Sample	Health effects tests	Ecological effects tests
Liquids	Ames, CHO	Aquatic, seed germination, nitrogen and seedling growth fixation
Solids (aqueous extract)	Ames, RAM, whole animal	Aquatic, seed germination, nitrogen and seedling growth fixation
Particulates	Ames, RAM, whole animal	Seed germination and seedling growth
Sorbent (extract)	Ames, CHO	Aquatic, seed germination, nitrogen and seedling growth fixation
Gases	Ames	Plant stress ethylene and foliar injury insect toxicity

TABLE 4. OPERATING CHARACTERISTICS OF WASTE TREATMENT SYSTEMS FOR TEXTILES

Assay	MAD	Range of concentration defining: High	Moderate	Low	Nondetectable (toxicity)
Ames	5 mg/plate or 500 μl	<0.05 mg <5 μl/plate	0.05-0.5 mg/plate 5-50 μl/plate	0.5-5 mg/plate 50-500 μl/plate	A negative response (see criteria) at a MTD or up to 5 mg/plate.[‡]
Rodent toxicity	10 mg/liter or 100%	<0.1 g/kg	0.1-1 g/kg	1-10 g/kg	LD_{50} at >10 g/kg or equivalent.
Fresh water and marine aquatic assays[§]	100 mg/liter or 100%	<1 mg/liter <10%	1-10 mg/liter 10-50%	10-100 mg/liter 50-100%	LD_{50} at > 100 mg/liter or 100%.
RAM	1,000 μg/ml or 600 μl/ml	<10 μg/ml <6 μl/ml	10-100 μl/ml 6-60 μl/ml	100-1,000 μg/ml 60-600 μg/ml	EC_{50} at >1,000 μg/ml or 600 l/ml.
CHO/WI-38 toxicity	1,000 μg/ml or 600 μl/ml	<10 μg/ml <6 μl/ml	10-100 μl/ml 6-60 μl/ml	100-1,000 μg/ml 60-600 μg/ml	EC_{50} at >1,000 μg/ml or 600 μl/ml.

[‡] Criteria for positive or negative interpretation of the Ames test are given in Appendix C.

[§] MAD for aquatic studies is set at 100 mg/liter or 100% if the total sample concentration is less than 100 mg/ml. Compound solubility can be used to set an upper limit in this assay.

Notes: MAD = Maximum Applied Dose
MTD = Maximum Tolerated Dose
LD_{50} = Lethal Dose 50%
EC_{50} = Effective concentration (50% may be substituted).

will be defined as having low toxicity. The degree of any concentration procedure will be factored into the calculation procedure and will reduce the level of toxicity accordingly.

Moderate—a significant response or an LD_{50} (EC_{50}) value ranging from a concentration less than 1/10 of the MAD (the lower limit of the low toxicity) to 1/100 of the MAD. Again using the same illustration, an LD_{50} (EC_{50}) obtained at a concentration ranging from 0.1 g/kg to 1.0 g/kg in the rodent toxicity assay will be considered as moderate. The same considerations of sample concentration will apply.

High—a significant response or an LD_{50} (EC_{50}) value less than 1/100 of the MAD for the particular assay. Thus, any sample with an LD_{50} less than 0.1 g/kg in the rodent assay will be considered to have high toxicity.

THE PILOT STUDIES

Most short-term bioassays employed in the Level 1 environmental assessment program were developed for testing relatively "pure" compounds. Their reliability for testing complex mixtures was not known. It was decided, therefore, to test the feasibility of biotesting of industrial samples in pilot studies.

Samples from three industries—textile wastewater, fluidized-bed combustor, and coal gasification—were evaluated in these pilot studies. The contract laboratories and EPA technical advisors involved in conducting these pilot studies are listed in Figure 1. The details of bioassay protocol, data interpretation, and data evaluation are presented elsewhere in this document. Only the overall summary and conclusions from the application of the short-term Level 1 bioassay matrix are presented here.

- Biological activity, especially genetic activity, may be masked by toxicity and may require chemical fractionation in order to demonstrate activity in the sample.
- For liquid affluents, tests for potential ecological effects may be more sensitive than tests for potential health effects due to concentration dilution problems.
- The prediction of relative toxicity on the basis of chemical analysis alone is subject to error.
- Results of biological and chemical tests are complementary—considered together the two types of tests provide useful information not obtainable when considered separately.

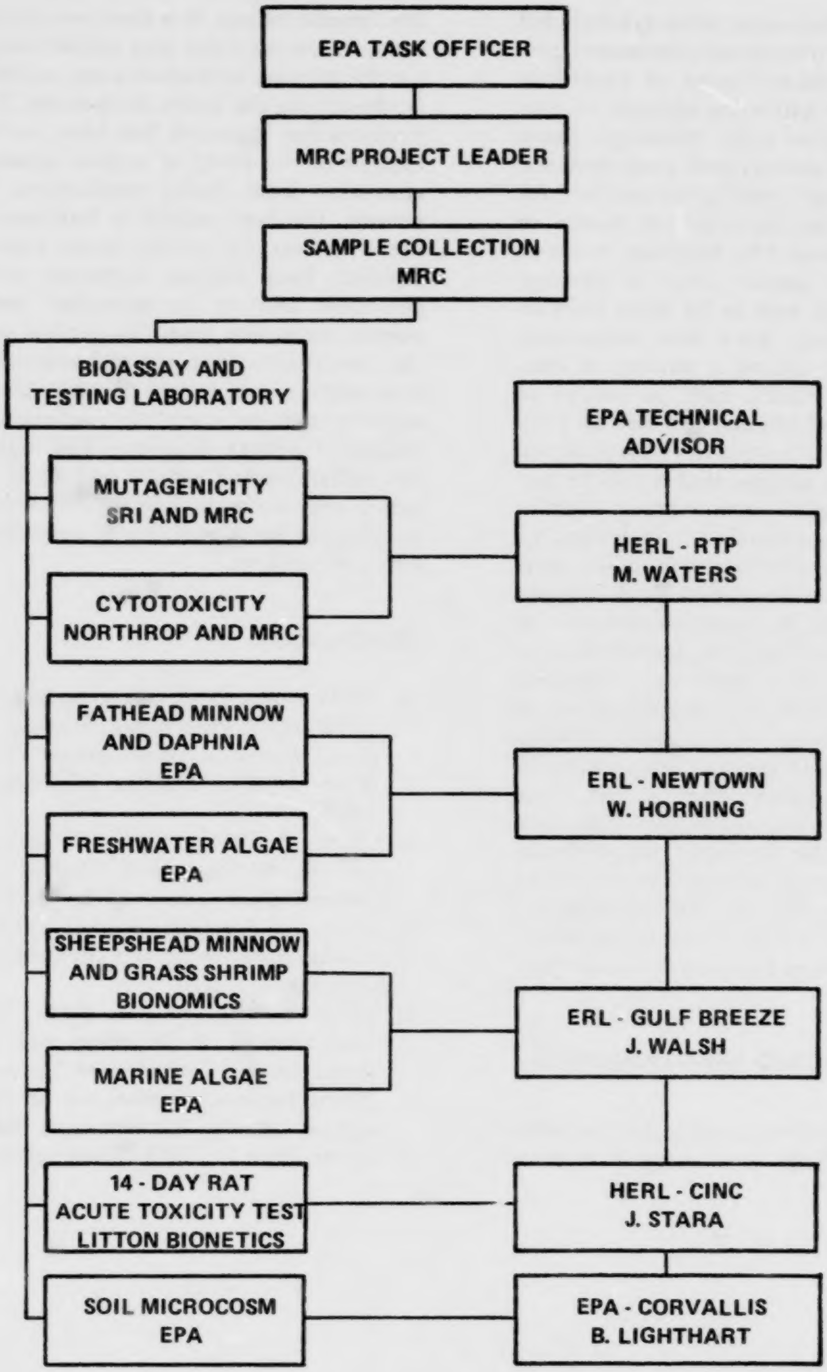

EPA TASK OFFICER
MRC PROJECT LEADER
SAMPLE COLLECTION MRC
BIOASSAY AND TESTING LABORATORY
MUTAGENICITY SRI AND MRC
CYTOTOXICITY NORTHROP AND MRC
FATHEAD MINNOW AND DAPHNIA EPA
FRESHWATER ALGAE EPA
SHEEPSHEAD MINNOW AND GRASS SHRIMP BIONOMICS
MARINE ALGAE EPA
14 - DAY RAT ACUTE TOXICITY TEST LITTON BIONETICS
SOIL MICROCOSM EPA
EPA TECHNICAL ADVISOR
HERL - RTP M. WATERS
ERL - NEWTOWN W. HORNING
ERL - GULF BREEZE J. WALSH
HERL - CINC J. STARA
EPA - CORVALLIS B. LIGHTHART

Figure 1. Laboratories and EPA technical advisors involved in biotesting of effluent samples in pilot studies.

RELIABILITY OF LEVEL 1 BIOASSAYS

The utility of short-term bioassays included in the Level 1 environmental assessment program is for the identification of hazardous streams and to prioritize the streams for further testing in higher order bioassays, based on positive results across Level 1 test systems. The data from Level 1 testing are not used for making decisions on the extent of hazard or safety of the streams. The bioassays included in Level 1 are in various stages of development. Some of them, such as the Ames *Salmonella*/microsome assay, have been reasonably well validated for testing a variety of compounds; whereas others, such as assays to evaluate terrestrial effects, are not as fully developed. The results from the pilot study on textile wastewater suggest that it may be necessary to concentrate certain liquid samples before these can be subjected to biotesting by in vitro techniques. The nature of in vitro procedures dictates the use of very small aliquots of aqueous samples. In a complex mixture the bioactive components may be present in very small amounts. Then detection, therefore, becomes difficult because of the limitations of the bioassay. To obtain reliable results from in vitro tests, the liquid samples frequently will have to be concentrated before testing. Also, especially for the in vivo range-finding rat test, the possible need for bioconcentration should be considered. The test animals should receive a daily dose of the test material rather than a single quantal dose as suggested in the *IERL-RTP Level 1 Bioassay Procedures Manual* (ref. 1).

BIOASSAY-DIRECTED FRACTIONATION

It may be difficult to detect and/or delineate the biological effects of a complex mixture without separating it into subfractions because the active compounds may be present in very low concentrations. It is therefore desirable to separate the mixtures into similar components for the purpose of concentrating and eventually identifying the active compounds. A limited fractionation approach has been successfully applied to the study of synfuel products and emissions from diesel combustion. In this scheme, the test sample is fractionated into four fractions; i.e., acidic, basic, neutral, and residual. Each fraction is further tested for genotoxic activity in microbial tests. The overall conclusion from the synfuel studies is that the results from the unfractionated complex mixture sample may be misleading. In the majority of cases, cumulative activity of the individual fractions is several fold higher than the unfractionated sample (ref. 3). It is anticipated that a simple fractionated scheme will be adopted for biotesting of industrial effluents and streams.

REFERENCES

1. K. M. Duke, M. E. Davis, and A. J. Dennis, *IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests for Pilot Studies,* EPA-600/7-77-043, 1977.
2. James A. Dorsey, Larry D. Johnson, Robert M. Statnick, and Charles H. Lockmüller, *Environmental Assessment Sampling and Analysis: Phased Approach and Techniques for Level 1,* EPA-600/2-77-115, June 1977.
3. M. D. Waters and J. L. Epler, "Status of Bioscreening of Emissions and Effluents from Energy Technologies," presented at Third National Conference on the Interagency Energy/Environment R&D Program, June 1-2, 1978, Washington, DC.

THE TESTING OF ENVIRONMENTAL SAMPLES FOR MUTAGENICITY AND CARCINOGENICITY USING MICROBIAL ASSAY SYSTEMS

Larry D. Claxton, Joellen Huisingh, Michael Waters*

Abstract

This paper will present a brief description of several microbial assay systems for mutagenicity and DNA damage. Using the Salmonella mutagenicity assay, an attempt will be made to identify and discuss the technical difficulties encountered in the screening of complex environmental samples. A second objective is to present available procedural modifications together with the utility of these modifications. The reproducibility and interpretation of the data from short-term bioassays will be discussed.

INTRODUCTION

It has been reported that over 4 million distinct chemicals are now known and that 63,000 chemicals are thought to be in common use (ref. 1). Trying to determine the public health effects of such a large number of chemicals is a massive undertaking (ref. 2). Microbial mutagenicity assays are now being used to identify agents showing genetic activity and as a carcinogen prescreen. A variety of short-term tests are available; however, the Salmonella mutagenicity assay has been the most extensively used. This paper will explore the basic protocol, precautions, and modifications (Ames) of the *Salmonella typhimurium* mammalian microsome assay. The application of this assay to complex mixtures such as industrial emissions and effluents will be discussed and methods of concentration, extraction, and fractionation will be considered. Since interpretation of results may sometimes be difficult, some discussion will concern the presentation and interpretation of data. Although the discussion will be mainly limited to the Salmonella assay, many of the considerations can be applied to other in vitro tests for mutagenicity.

THE BASIC SALMONELLA PLATE INCORPORATION TEST

The reference protocol is described by Ames et al. (ref. 3) and will not be repeated here. The outline of the basic procedural protocol is a very simple one (Figure 1). Basically, a specific amount of the chemical to be tested and a mixture of the indicator bacterial strain are added to melted soft agar, mixed, and poured into a minimal media plate that will select for bacteria that have undergone mutation. The plate is incubated for 48 hours at 37° C and then scored for the number of colonies per plate. This procedure is repeated for each dose of the chemical; for each bacterial strain; for each routine modification (e.g., with and without microsomal activation); for each needed control; and for each duplication. Therefore, a chemical tested at 5 doses, with 3 replicate plates at each dose, with 5 bacterial strains, with appropriate controls, and done both with and without microsomal activation, will cause this basic procedure to be repeated a minimum of 210 times, thus generating 210 "data points" for each chemical to be analyzed.

The procedure scores for gene mutations that occur in the histidine locus in strains of *Salmonella typhimurium* created by Dr. Bruce Ames. Each of these strains has undergone a specific mutation within the histidine locus and thus is unable to grow unless histidine is supplied. These strains are said to have a histidine-negative genome (his –). When these strains mutate to a histidine-positive genome they can be detected on a nutrient medium that lacks histidine. Since these strains are "mutating back" to a wild type condition, a reverse mutation is said to occur; however, the biochemical mechanisms are the same as occur in forward mutation. Systems that detect forward mutation, though, are generally not limited to a specific type of genetic event (e.g., a frameshift or a point mutation), whereas a reverse mutation system does detect a specific

---

*Biochemistry Branch, U.S. Environmental Protection Agency, Environmental Toxicology Division, Health Effects Research Laboratory, Research Triangle Park, NC.

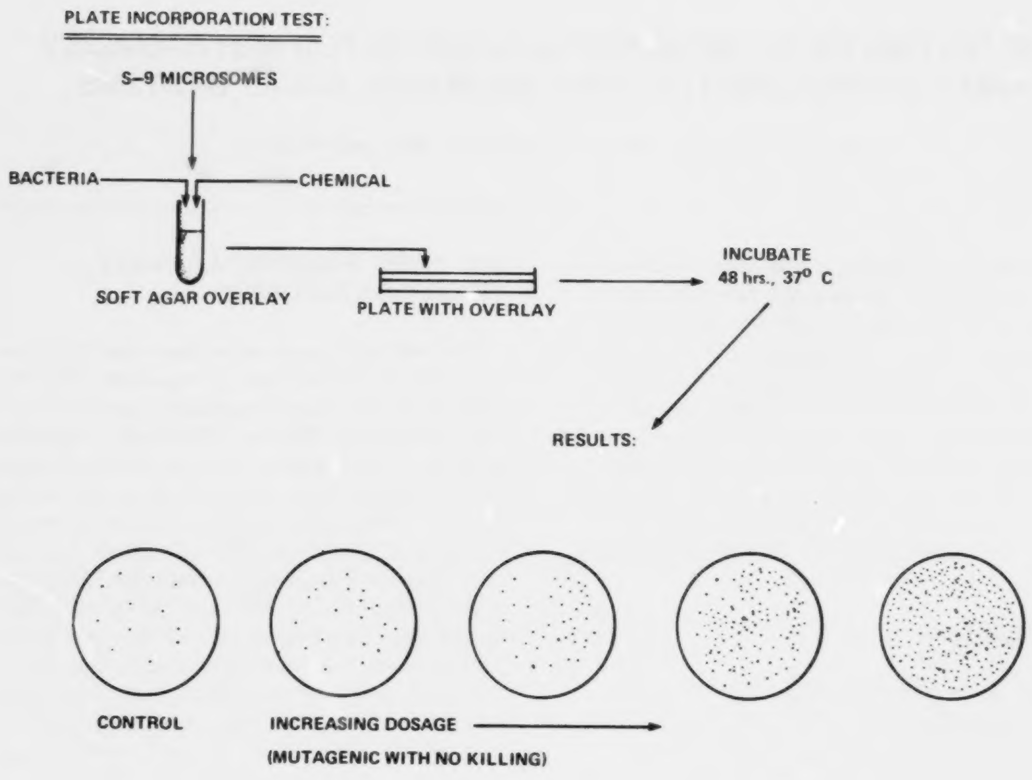


Figure 1. Outline of basic procedural protocol.

type of mutation. Since screening systems need to score for a variety of genetic mutational events, several different Salmonella strains have been developed. Each strain detects a specific type of mutation and incorporates other changes needed to increase its sensitivity. There are now five strains in common use (Table 1). Three of these strains (TA1537, TA1538, TA98) detect frameshift mutations. TA1537 detects compounds such as 9-aminoacridine. TA1538 and TA98 both detect compounds such as 2-nitrosofluorenone, but differ in the fact that TA98 contains an R factor plasmid. Chemicals that produce base-pair substitutions, especially alkylating agents, are detected in TA1535. Strain TA100 was developed from TA1535 by the addition of the R factor plasmid. TA100 has a rather high spontaneous mutation rate and may detect chemicals that normally yield frameshift mutations as well as base-pair substitutions.

In addition to the histidine locus alteration, these strains carry an rfa mutation that creates a deficiency in the bacterial cell wall lipopolysaccharides. This deficiency increases the cell's permeability to large molecules. The uvr B mutation was added to these strains to increase their susceptibility to several classes of mutagens by decreasing genetic repair. The R factor plasmid found in strains TA98 and TA100 increases further the sensitivity of the tester strains by participating in a type of error-prone repair. The plasmid is detected by ampicillan resistance. These strains also differ in the number of spontaneous revertants per plate generally found. Table 1 summarizes the characteristics of the five strains.

TABLE 1. CHARACTERISITICS OF FIVE SALMONELLA TYPHIMURIUM TESTER STRAINS

Strain	his-mutation	rfa	uvr B	R factor	Spontaneous revertants/plate
TA1535	*his* G46	Yes	Yes	No	5-50
TA1537	*his* C3076	Yes	Yes	No	2-25
TA1538	*his* D3052	Yes	Yes	No	5-40
TA98	*his* D3052	Yes	Yes	Yes	15-75
TA100	*his* G46	Yes	Yes	Yes	80-200

MAMMALIAN METABOLIC ACTIVATION

Some compounds that are carcinogenic for mammals are not mutagenic for bacteria; therefore, a mammalian metabolic activation system has been added to the assay. This addition allows for some of the metabolites as well as the agent itself to be tested for mutagenicity. The activation system described by Ames consists of a 9,000 × g supernatant of a rat liver homogenate. Aroclor induction of the rats is done in order to induce the hepatic enzymes referred to collectively as mixed function oxygenases (MFO). An induced MFO system gives the potential for increased levels of metabolites and a corresponding increase in revertant colonies due to mutagenic metabolites.

PRECAUTIONS AND PROCEDURAL MODIFICATIONS

Although the reference protocol has been described in great detail, separate laboratories may make certain modifications to meet special needs. The authors will attempt to describe procedures likely to be neglected or altered and the potential effects this is liable to have on the reliability of the generated data. This should be helpful to both the laboratory investigator using the test and the reviewer who examines only the results. The points considered will follow as closely as possible the sequence encountered within a testing protocol.

Checking of Tester Strains

Upon the receipt of tester strains and at regular intervals, the tester strains should be checked for UV sensitivity, ampicillan resistance, and crystal violet killing. A failure to check these parameters could allow for mixed cultures and decreased sensitivity or false negatives and positives. If these parameters are not checked, the test should be considered unacceptable. Although spontaneous and positive controls are conducted with each test, the invalidating of some tests can be prevented by checking spontaneous and induced mutant levels when creating master plates.

Proper Overnight Culture Growths

Variation between bacterial strains, media used, and testing conditions can cause considerable variation in the bacterial culture used for testing. Three conditions should always be met for the routine screening of chemicals. First, a single colony isolate should be used to initiate the culture. This helps to insure genetic uniformity of the broth culture. Second, the test culture should have a concentration of 1 to 2 × 10^9 viable cells per milliliter. Note that it is viable cells per milliliter. This can best be insured by using the culture in the early portion of the stationary growth phase. Next, if cells cannot be used immediately upon harvesting, they should be stored in an ice-water bath.

Mammalian Activation System

For general screening the 9,000 × g supernatant (S9) from rat liver induced with Aroclor 1254 is generally recommended. This is an area of the protocol that can be modified in a variety of ways. One may modify the organism (rat, mouse, guinea pig, plant, bacterial flora, etc.); the tissue source (skin, liver, kidney, embryoes, etc.); the biochemical fraction (S9, purified microsomes, etc.); induction chemicals (Aroclor, phenobarbitol, ethanol, etc.); and the induction schedule. One may also use in vivo activation by examining the urine or bile of treated animals.

These modifications are not generally applied. However, there are typically two indications for using one or more of these modifications. First, if the route of exposure or the concentration of the substance is associated with a specific organ, that tissue could be used in addition to liver. Second, when compounds of like chemical structure are shown to be positive only when one of these modifications is used, that modification should be used. As an example, since human exposure to flame retardants occurs via the skin, Rosenkranz tested the activation of tris (2,3-dibromogropyl) phosphate ("Tris") using skin enzymes (ref. 7). He found that the skin of newborn animals was capable of transforming "Tris" to a mutagenic intermediate and that this activity was enhanced by inducers such as Aroclor.

The Substance to be Tested

The test sample brings the greatest variability into the test system; therefore, the effects of the substance tested should be closely defined. First, an adequate number of concentrations and range of concentrations should be tested. With the initial screening of a substance, at least five doses at half-log intervals should be tested if possible. Compounds demonstrating little or no toxicity should preferably be tested in the 5- to 10-mg per plate range before being reported as negative.

The solubility of the test substance should be noted when placed both into the solvent and into agar overlay. The precipitating of substances may not allow for adequate testing. Highly volatile substances may evaporate so quickly that they are not adequately tested. These volatile substances should be tested in sealed bags or dessicators.

Some indication of the toxicity should be recorded. For example, if clearing of the test plates is seen at all doses, lower doses should be tested in order to assure that the effect seen is not due to toxicity. Also, a negative mutation response when no toxicity is seen is a questionable result. When toxicity does result, some of the bacteria may lyse and contribute histidine to media; therefore, cross feeding may result and colonies that are not revertants may be found. Usually these colonies are small pinpoint colonies, yet that is not always the case. Colonies from representative plates should be transferred to minimal media plates without histidine to insure that they are revertant colonies. Replica plating is an excellent means of accomplishing this check.

Other substances, especially complex mixtures and technical-grade chemicals, may either contain histidine or histidine-like-acting components. Strain TA100 is especially sensitive to small increases in histidine. One should determine if the test substance is related to a known compound that has been previously tested. Some chemical classes (such as the low-molecular-weight nitrosamines) are known to give negative results in the typical plate incorporation test. Either a modification of the Salmonella test or another bacterial species should be used under these circumstances.

Within-Experiment Controls

Every test should contain appropriate positive, negative, and sterility controls. Table 2 records some of the acceptable positive controls for the five commonly used tester strains. The negative control should consist of the entire system without the compound to check spontaneous mutation rate. The activation mix and test substance should be checked for sterility.

Minimal Design Criteria for Assigning a Negative Response to the Plate Test

Since most positive results are easily distinguished, the experimental design should be done to give some definition to a negative result. In the authors' opinion the following are the minimal testing requirements needed to operationally designate a test negative. (More will be said about defining a negative in a later section.)

- Minimal of five doses at half-log intervals, with the highest dose being highly toxic or presented at a minimum of 5 mg per plate;
- Spontaneous and positive controls done at least in duplicate;

TABLE 2. CONTROL MUTAGENS

Strain	Without activation	With activation
TA 1535	MNNG, or sodium azide, or methylmethane sulfonate	2-Anthramine
TA 1537	9-Aminoacridine	2-Anthramine
TA 1538	2-Nitrofluorene, or	2-Anthramine
	4-Nitro-o-phenylenediamine	2-Anthramine
TA 98	2-Nitrofluorene, or hycanthone methanesulfonate	2-Anthramine
TA 100	MNNG, or sodium azide, or MMS, or nitrofurantoin	2-Anthramine

- Positive controls (in duplicate) for any bacterial/microsomal activation combination used;
- At least two replicates per dose;
- At least one replicate experiment, if possible, done with a narrower dose range;
- Tested in TA1535, TA1537, TA1538, TA98, TA100 (this requirement may change with the development of new strains and/or data);
- Proper sterility controls; and
- Checking of colonies for genotype.

Procedural Modifications Possible

Spot Test—

This is a very qualitative form of the plate test where bacteria and the activation system (if used) are overlayed onto a minimal media plate and the chemical is spotted onto the plate or onto a paper disc on the plate. This test is used for rapid screening of many compounds or for substances limited by availability. The diffusibility of the substance strongly influences the results (ref. 3).

Well Test—

The well test is a modification of the spot test, which is to be used where the supply of the sample is very limited. After the bacteria are overlayed, wells are cut in a specified pattern. Into each well soft agar with either the activation system, the positive control, the control solvent, or a test substance is placed. The advantage of the well test is that one or two substances can be placed, along with controls, on a single plate for mutagenicity both with and without activation. Diffusibility again is the main limiting factor and the results are only qualitative (ref. 5).

Liquid Suspension Assay—

This is a more quanitative test than the plate test; however, it is much more time consuming and costly. Incubated together in a buffered suspension are the bacteria, any activation system used, and the compound used. After a specified time of exposure, aliquots are transferred to appropriate plating media to score for both survival and revertant colonies. This procedure gives an approximation of actual mutation frequency (ref. 6).

Preincubation Test—

Performed otherwise in the same manner as the plate test, the preincubation test also requires that the bacteria and chemical be preincubated together at room temperature, 37° C, or 45° C before soft agar is added and plating is done. This modification allows for the detection of mutagenicity in some compounds that are not detected in the plate test, and it is a less complex test than the liquid suspension assay (ref. 7).

Fluctuation Test—

Bacteria are incubated in suspension with the test substance without histidine, and the number of tubes demonstrating growth are scored. This is a very sensitive system for detecting some mutagens and is amenable to automation (ref. 8).

Anaerobic Testing—

The plate test is performed and the plates incubated in Gas Pak jars in the dark at 37° C for 14 hours and then incubated aerobically. Certain chemicals (e.g., aga thioprine) can be demonstrated as mutagenic only in this way (ref. 4).

Host-Mediated Assay—

With this protocol, the bacterial indicator organism and the substance to be tested are administered to a mammal via different routes. After a specified period of time, the bacteria are recovered and handled as in a liquid suspension test. Although the substance is distributed and metabolized throughout the whole body, a variety of technical problems complicate the test. These include: bacterial recovery, bacterial-metabolite proximity, immune response to bacteria, etc. (ref. 9).

Special Procedures for Complex Mixtures

Complex mixtures present a variety of technical difficulties but are quite capable of being tested. Most complex mixtures are direct environmental pollutants and include a diversity of sample types. Some of these samples are very low in organics while others are entirely organic.

Liquid secondary effluents from 22 textile plants were initially tested without concentration or extraction with four Salmonella strains and in a battery of other microbial bioassays (ref. 10). No positive mutagenic response was detected for any of these samples. Quantitative chemical analytical data on selected organics showed the presence of suspected carcinogens and mutagens; the concentrations of these chemicals in the effluent, however, were below the concentration expected to be detectable in the Salmonella assay (ref. 10).

The mutagenic activity of a complex mixture may not be detectable to a variety of problems. Examples of these would be: (1) dilution (as in the textile wastewater example); (2) presence of a sample matrix which prevents release of the mutagens into the bacterial media (as in the case with certain carbonaceous particulate samples), or (3) the presence of highly toxic compounds in the mixture—which results in sufficient bacterial killing to prevent detection of bacterial mutants. To overcome these problems, complex mixtures must often be concentrated, extracted, or fractionated prior to bioassay. Model applications of these method are described below.

Concentration—

There are a variety of methods by which samples can be concentrated. If the sample is particulate or precipitates out of the solvent used, filtration will concentrate the sample. The type of filtration will depend upon the sample. For example, air particulates are usually filtered by the use of polflex or glass fiber filters. Some water and solvent samples can be filtered for particulates with Millipore and Nucleopore filters and other similar filters. Air particulates also may be concentrated by impaction devices and electrostatic precipitation. Water and other fluid samples have been concentrated by chromatography methods. The XAD® columns appear to be especially suited to water and urine samples (refs. 11,12,13). The researcher needs to realize that concentration may enhance chemical reactions between the constitutents of a complex mixture and thereby influence bioassay results.

Extraction—

Active organic compounds may be attached to a variety of solid materials. Since bacteria cannot ingest most of these solid materials (as some mammalian cells are able to), the organics must be extracted from the solid matter. A variety of solvent systems have been used including benzene, dichloromethane, cyclohexane, acetone, methanol, methanol-benzene, and dimethyl sulfoxide. Sonication along with a solvent system has also been used. Usually the mixture must be solvent exchanged before testing in the Ames test. These approaches to evaluating the organics associated with air, industrial, and mobile source particulates were recently reviewed (ref. 14).

Extraction has not been as extensively applied to liquid samples. However, Kulik (ref. 15) has applied this approach to several selected secondary effluents from the textile plants referred to above. When any of these methods are used, several questions must be addressed. What types of compounds are extracted and are not extracted by the procedure? Does the solvent interact with any of the compounds to produce artifactual components? When the solvent itself is mutagenic, has it been effectively removed before testing? What special controls should be used with testing?

Fractionation— Epler (ref. 16) has shown that the mutagenic activity of some complex mixtures cannot be detected until the mixture is fractionated. This appears to happen because toxic components of the complex mixture are removed by fractionation.

Safety Precautions

The following is a listing of some safety procedures established within the author's laboratory.

1. All samples for testing and positive control chemicals are housed in a special weighing and storage area. These samples and chemicals are recorded and logged in and out.
2. All weighings and measurings of stock chemicals are handled in a special weighing room within glove boxes that are vented to the outside through charcoal filters located on the roof.
3. Incubators, storage cabinets, and refrigerators are vented. Upon the opening of any of these units the air within the unit is exhausted.
4. All work is performed in laminar-flow exhaust hoods or total-exhaust biological hoods.
5. All work is done in designated areas by employees properly clothed with disposable clothing.
6. No mouth pipetting is allowed for any procedure.
7. All waste is double bagged and then placed in drums which are sealed and sent by a contractor to special landfill areas for disposal.

Data Interpretation

Since actual mutational frequencies cannot be calculated with the plate test, disagreement exists as to the best statistical methods to employ. The following, however, should be reported and evaluated for ideal judging of the adequacy of a test:

- proper controls—positive, negative, sterility;
- solubility and stability of test chemical;
- replication of plates at each dose and replication of each test;
- the number and range of doses used;
- the toxicity of the sample;
- contamination of the sample;
- relatedness of sample to other known compounds;
- proportionate increase of individual doses above spontaneous levels; and
- presence or absence of dose response curve.

In order to say that a definite positive has been seen in the author's laboratory, the following is expected:

- at least a 2.5-fold increase at one or more doses;
- a dose response curve with some type of "regular curve"—i.e., a single high response would not be accepted;
- expected responses from all controls; and
- apparent absence of histidine cross feeding and/or contamination.

A dose response increase seen with proper controls but never reaching a 2.5-fold increase is considered questionable.

One may present summarized data in a variety of ways. It has been suggested, however, that summarized data not be given without its supporting data (ref. 17). Some of the methods for data presentation follow.

1. Fold increase or mutagenic index—average plate counts divided by average spontaneous count for the same bacterial strain;
2. Net increase in revertants—average counts or individual counts minus average spontaneous count (this is generally considered unacceptable);
3. Specific activity—slope of the linear portion of the dose response curve at a specified dose (e.g., 1 mg);
4. Specific activity fold increases—the specific activity divided by the average spontaneous count;

5. Specific response activity—calculated dose needed to give a specific number of revertants per plate (e.g., 200 revertants/plate) for a specific strain;
6. Maximum response—maximum number of revertants per plate seen.

These methods are used to compare the results of a series of tests but do not necessarily reveal the adequacy or positiveness of the results. A generally accepted statistical test for examining the results of the Salmonella plate test has not been published and until this occurs, people will be forced to examine the data by these less exacting means.

REFERENCES

1. Thomas H. Maugh, "Chemicals: How Many Are There?" *Science*, Vol. 199, No. 4325, p. 162, 1978.
2. Larry D. Claxton and Patricia Z. Barry, "Chemical Mutagenesis: An Emerging Issue for Public Health," *American Journal of Public Health*, Vol. 67, No. 11, pp. 1037-1042, 1977.
3. Bruce N. Ames, et al., "Methods for Detecting Carcinogens and Mutagens With the Salmonella/Mammalian-Microsome Mutagenicity Test," Mutation Res., Vol. 31, pp. 347-364, 1975.
4. Herbert S. Rosenkranz, et al., "The Use of Microbial Assay Systems in the Detection of Environmental Mutagens in Complex Mixtures," *Application of Short Term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures*, M. Waters et al., eds., U.S. EPA, 1978, in press.
5. Thomas J. Hughes, et al., "Agar Diffusion Well Test for Mutagenic Screening of Air Particulates," 1978, in review.
6. C. N. Frantz and H. V. Malling, "The Quantitative Microsomal Mutagenesis Assay Method," *Mutation Res.*, Vol. 31, No. 6, pp. 365-380, 1975.
7. T. Yahagi, M. Nagao, Y. Seino, T. Matsushima, T. Sugimura, and M. Okada, "Mutagenicity of N-nitrosamines on Salmonella," *Mutation Res.*, Vol. 48, pp. 121-130, 1977.
8. M. H. L. Green, A. M. Rogers, W. J. Muriel, A. C. Ward, and D. R. McCalla, "Use of a Simplified Fluctuation Test to Detect and Characterize Mutagenesis by Nitrofurons," *Mutation Res.*, Vol. 44, pp. 139-143, 1977.
9. H. V. Malling, "The Host-Mediated Assay," Proceedings of the Fourth International Congress, Motulsky and Lentz, eds., pp. 207-211, 1973.
10. D. C. Poole, and V. F. Simon, final report of "In Vitro Microbiological Studies of Twenty-two Wastewater Effluent Samples Reported in Source Assessment: Textile Plant Wastewater Toxics Study Phase I," EPA Publication 600/2-78-004h, March 1978.
11. E. Yamasaki and B. N. Ames, "Concentration of Mutagens From Urine by Absorption With the Nonpolar Resin XAD-2: Cigarette Smokers Have Mutagenic Urine," *Proc. Natl. Acad. Sci. USA*, Vol. 71, No. 8, pp. 3555-3559, 1977.
12. C. C. Smith, "Strategy for Collection of Drinking Water Concentrates: Application of Short-term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures," EPA Publication 600/9-78-027, pp. 227-246, September 1978.
13. C. D. Chriswell, B. A. Glatz, J. S. Fritz, and H. S. Svec, "Mutagenic Analysis of Drinking Water," EPA Publication 600/9-78-027, pp. 447-494, September 1978.
14. M. D. Waters, S. Nesnow, J. L. Huisingh, S. S. Sandhu, and L. Claxton, eds., "Application of Short-term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures," EPA Publication 600/9-78-027, September 1978.
15. F. A. Kulik, "Concentration of Potential Mutagenic Compounds in Textile Plant Effluents for Application to the Salmonella Mutagenicity Test," EPA Publication 600/9-78-027, p. 584, September 1978.
16. J. L. Epler, B. R. Clark, C-h. Ho, M. R. Guerin, T. K. Rao, "Short-term Bioassay of Complex Organic Mixtures: Part II, Mutagenicity Testing," EPA Publication 600/9-78-027, pp. 269-290.
17. NIEHS-sponsored conference, "Salmonella/Microsome Assay—Workshop on Data Production and Analysis," Meeting Report, 1978, in preparation.

CELLULAR TOXICITY OF LIQUID EFFLUENTS FROM TEXTILE MILLS

James A. Campbell,* Neil E. Garrett,*
Joellen L. Huisingh,† Michael D. Waters†

Abstract

The rabbit alveolar macrophage (RAM) short-term bioassay was used to determine the cellular toxicity of 23 water samples containing textile mill effluents. WI-38 human lung fibroblasts and Chinese hamster ovary (CHO) cells were used for comparative cytotoxicity studies. Parameters examined in estimating cellular toxicity included: viability by trypan blue dye exclusion; cell numbers by optical enumeration; cellular ATP by luminescence assay; and clonal growth in CHO cells. Less than 10 percent of the textile mill effluent samples studied measurably affected macrophage viability. Approximately 30 percent significantly affected total ATP of the macrophage. RAM and WI-38 cells responded similarly to a selected sample of four effluents. Cellular ATP content in the RAM and WI-38 was a sensitive index of toxicity. In general, CHO clonal growth was a more sensitive index of toxicity than ATP content of either the RAM or WI-38.

INTRODUCTION

In vitro testing of environmental effluents from manufacturing processes can be performed in a wide variety of biological systems. The parameters evaluated in determining cellular toxicity frequently include morphological changes detectable by light and electron microscopy, alteration in cell growth and division, biochemical alterations, and cytochemical changes. In many cases environmental toxicants exert their effects through complex and indirect mechanisms. Primary cell cultures, such as the macrophage, exhibit many of the metabolic and functional attributes of the original in vivo state. The rabbit alveolar macrophage has been used to evaluate the toxicity of a variety of environmental agents including gases (refs. 1,2), salts of soluble metals (refs. 3,4,5), metal oxides (refs. 5,6), and environmental particulates (ref. 7). Chemical analysis has revealed a complex mixture of organic and metallic compounds in liquid effluents from textile mills. The objective of this study was to examine the potential applicability of the RAM system to determine the relative cellular toxicity of 23 water samples containing textile mill effluents. In order to compare the cytotoxic responses in different cell types, four of the textile mill effluents were also evaluated using the diploid WI-38 human lung fibroblast and the aneuploid CHO cell. Toxicity of the effluents was evaluated in cultures of macrophages or WI-38 cells after exposure for a 20-h period. After incubation, cell number, viability, and cellular adenosine triphosphate (ATP) were measured in control and treated cultures. Toxicity of the effluent samples to the CHO cell was evaluated by counting the number of colonies formed after a 6-day exposure period.

METHODS

Sample Handling

Liquid samples were stored at 4°C and tested at concentrations of 1 to 600 μl/ml in culture medium. Dilutions were made with supplemented culture media, sample, and/or sterile distilled water to maintain proper isotonicity. Samples were filtered through a 0.45 μ Millipore filter prior to testing. Experiments were performed which indicated that toxicity observed from filtered and unfiltered samples was approximately equivalent.

Before cytotoxicity testing of unfiltered samples, an antibiotic sensitivity test was conducted to ascertain if antibiotics were needed to suppress growth of any bacteria in the sample. Nutrient agar plates were streaked with 0.5 ml of sample and antibiotic sensitivity disks were added for a 24-h incubation period.

---

*Northrop Services, Inc., Cytotoxicity and Biochemistry Section, Environmental Sciences Group, Research Triangle Park, NC.

†U.S. Environmental Protection Agency, Biochemistry Branch, Environmental Toxicology Division, Health Effects Research Laboratory, Research Triangle Park, NC.

The antibiotics present in the culture medium were capable of inhibiting bacterial growth.

RAM Testing Procedure

Procurement of Macrophages and Treatment of Cultures—

New Zealand white rabbits of both sexes were used. Clinically healthy animals were sacrificed by means of 150-mg injections of sodium pentobarbital into the marginal ear vein. Tracheostomies were performed using sterile operating procedures. Lung lavage was performed in situ (ref. 1). Thirty ml of 0.85 percent saline (23°C) was introduced into the lungs and allowed to remain for 15 minutes. After removal of this initial lavage fluid, five subsequent infusions were introduced and removed immediately. Lavage fluid found to contain blood or mucous was discarded. The cells were washed once in normal saline by centrifugation at 450 × g for 15 minutes at 0° to 4°C. After a second centrifugation, the cells were resuspended in tissue culture Medium 199 with Hanks Salts (0° to 4°C). All media and sera were obtained from Grand Island Biological Company, Grand Island, NY. Media was supplemented with 10 percent heat-inactivated fetal calf serum, 100 units/ml penicillin, and 100 μg/ml streptomycin and kanamycin. Cells were counted and viability determined by means of a hemocytometer or Biophysics Cytograf. The cell suspension was then diluted to 2.0×10^6 cells per milliliter. If cell viability was less than 90 percent the cells were not used. A differential cell count was performed with a minimum of 200 cells being scored.

Liquid samples in media (total volume of 1.5 ml) were then added to each of three cluster dish wells, followed by 0.5 ml of supplemented Medium 199 (10 percent fetal calf serum and antibiotics) containing 2×10^6 cells per milliliter. No pH adjustment was made for the initial testing. If a sample, toxic at initial testing, caused a drop in pH below 6.8 or an increase above 7.6, the sample was retested under both pH-adjusted and unadjusted conditions. The adjustments were made using ultrapure HCl and NaOH to pH 7.2. After gentle mixing, the dishes were incubated on a rocker platform for a 20-h period at 37°C in a humidified atmosphere containing 5 percent CO_2 in air.

Harvest of Macrophages, Cell Enumeration, and Biochemical Analyses—

At the end of the incubation, media containing unattached cells was removed from each dish and maintained separately in an ice bath. The attached cells were removed with 1.0 ml/well of 0.25 percent trypsin and combined with the decanted media. One-tenth ml of the combined cell suspension was removed for ATP determinations, and 0.5 ml for viability and cell number measurement.

Viability was determined by trypan blue dye exclusion. For hemocytometer counts, 0.1 ml of 0.4 percent trypan blue was added to 0.5 ml of cell suspension and counted after 5 minutes. Simultaneous determinations of cell viability and cell numbers were made.

Adenosine triphosphate (ATP) was determined using a Du Pont Model 760 Luminescence Biometer according to a procedure supplied with the instrument. Briefly, dimethylsulfoxide (0.4 ml) was used to extract ATP from a 0.1 ml aliquot of trypsinized cell suspension. After 2 minutes at room temperature, 2.5 ml of cold 0.01 molar morpholinopropane sulfonic acid at pH 7.4 was added to buffer the extracted sample. The extract was then placed in an ice bath. Aliquots of 10 μl of each extract were injected into the luminescence biometer's reaction cuvette containing 0.7 millimolar luciferin, 100 units crystalline luciferase, 0.01 molar magnesium sulfate, and filtered deionized H_2 (total volume of 100 μl). Light emitted from the reaction cuvette was measured photometrically in the luminescence meter and was proportional to the ATP concentration of the sample.

Human Lung Fibroblast (WI-38) Assay

Human lung fibroblasts were obtained from the American Type Culture Collection, Rockville, Maryland. Cells were subcultivated twice weekly by use of 0.25 percent trypsin in GIBCO solution A at a 1:2 split ratio. Cultures were not employed beyond the 35th subcultivation. Cells were maintained in Basal Medium Eagle with Earle's Salts plus 10 percent fetal calf serum (virus screened) and 2 μmol/ml-glutamine. Cells maintained under these conditions showed a period of rapid growth from 24 to 72 hours after subcultivation, during which time the experiments were performed. Antibiotics were routinely removed from the maintenance cultures to determine the presence of contaminating microorganisms. For testing of environmental samples the media was further supplemented with 100 units/ml penicillin, 100 μg/ml streptomycin, and 2.5 μg/ml amphotericin B.

The WI-38 assay was performed by plating 2.5×10^5 cells/4 milliters into 25 cm^2 Falcon flasks and adding dilutions of the test sample 24 hours after the cells had adhered to the flask surface. Dilutions were made with 10X Eagle's Basal Medium, sample, and/or sterile distilled water to maintain proper isotonicity. The cultures were incubated with closed caps for 20 hours at 37° C. At the end of the incubation period, the cells were trypsinized and cell counts, cell viability, and ATP determinations performed as described previously for the RAM assay.

Chinese Hamster Ovary (CHO-KI) Clonal Cytotoxicity Test

The Chinese Hamster Ovary (CHO) cell line was obtained from the American Type Culture Collection and maintained in Ham's F-12 medium supplemented with 10 percent fetal calf serum (virus and mycoplasma screened). The cells were subcultured using 0.25 percent trypsin twice weekly and incubated at 37° C in plastic culture flasks.

The clonal assay using the CHO system involves plating of 200 to 300 cells per 25 cm^2 tissue culture flask. For evaluation of samples, F-12 media was supplemented with 10 percent FCS, 100 units/ml penicillin, 100 μg/ml streptomycin, and 2.5 μg/ml amphotericin B. Four-ml suspensions of CHO cells were added to flasks and the cultures incubated for 18 to 24 hours at 37° C to allow for cell attachment. Replicate flasks (3 per concentration) were then exposed to samples prepared in supplemented F-12 media. The cultures were then incubated at 37° C with closed caps and allowed to develop discrete colonies of cells. After 6 days the cultures were fixed with 10 percent formalin in 0.5 percent NaCl and 4.0 percent methanol for 30 minutes and stained with 0.04 percent crystal violet for 15 minutes. The flasks were then washed with deionized H_2 and allowed to dry. Colonies were enumerated and the data expressed as a percent of the control value.

Mathematical and Statistical Analysis

Data from dose response experiments were used to determine an estimate of the sample concentrations needed to reduce cell viability and cell ATP content by 20 percent (EC_{20}) or 50 percent (EC_{50}). EC_{20} and EC_{50} values were obtained from the dose response relation by inverse prediction from the simple regression line. All dose response data were mathematically transformed and then fitted to a straight line by the method of least squares. Concentrations were expressed as the natural logarithm of the dose in μl/ml. Viability was transformed to the arc sine of the square root of the fraction of viable cells. ATP data expressed as a percent of control were fitted to a straight line with the logarithm of the dose. Confidence limits on the estimated EC_{20} and EC_{50} values were obtained using standard statistical procedures (ref. 8).

RESULTS AND DISCUSSION

The macrophage assay was used to evaluate the toxicity of 23 textile mill effluents. The response of RAM cells to a toxic effluent from textile mill wastewater (sample N) is shown in Figure 1. After a 20-h exposure period the effect on macrophage viability, viability index[‡] (ref. 3), ATP, and cell number was determined. Cell viability and viability index were reduced from 94 percent in control cultures to 58 percent and 62 percent, respectively, in cultures treated with 600 μl/ml of sample. Sample N was not appreciably cytolytic as evidenced by the fact that total cell number was not affected. Cellular ATP was the most sensitive parameter measured. In cultures treated with 600 μl/ml, ATP was reduced to 7 percent of the control value.

Dose response curves as illustrated in Figure 1 were obtained and the data were used to

---

[‡] The viability index is defined as:

$$\text{viability index} = \text{viability (\%)} \times \frac{\text{no. of cells in test culture}}{\text{no. of cells in control culture}} .$$

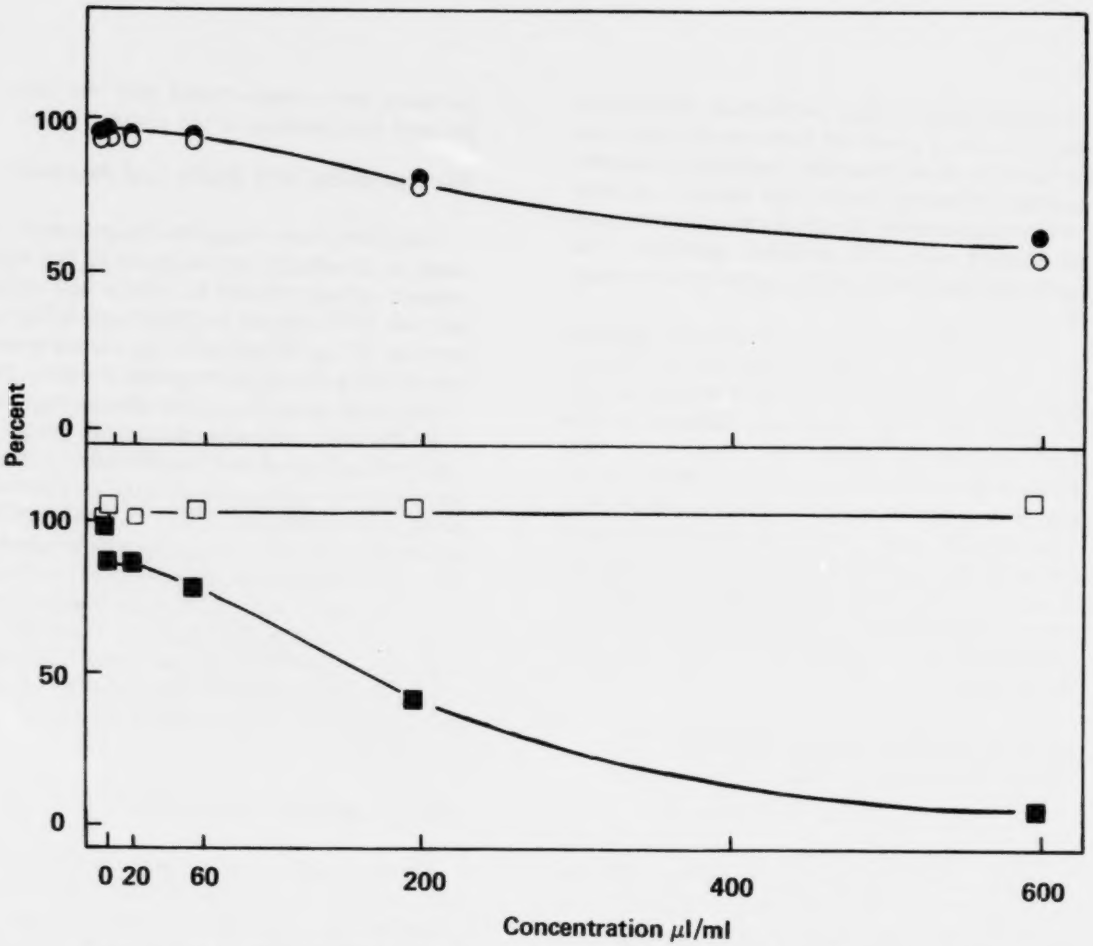


Figure 1. Response of rabbit alveolar macrophage to textile mill effluent sample N after a 20-hour exposure (● — ●, viability index; O — O viability; ☐ — ☐ cells/ml; and ■ — ■ ATP [fg/cell]). Cells/ml and ATP are expressed as the percent of the control value.

determine an estimate of the sample concentrations needed to decrease cell viability and cell ATP content by 20 percent (EC_{20}) or 50 percent (EC_{50}). Textile mill effluents for which either a 20 percent or 50 percent response could be determined are shown in Table 1. The EC_{20} and EC_{50} values are accompanied by the 95 percent confidence intervals. Only two samples, N and C, caused a significant reduction in cell viability. Duplicate experiments with sample N were performed. Two experiments were also performed with sample C. This sample increased the pH of the cell culture medium to 8.2 at 200 μl/ml and pH 9.1 at 600 μl/ml. In one of the experiments sample C was evaluated with the pH adjusted to 7.2 and no toxicity was detected.

As shown in Table 1, seven samples significantly reduced cell ATP content. This result indicated that ATP, as measured by luminescence assay, is a more sensitive index of cellular toxicity than is viability as determined by trypan blue dye exclusion. Three samples, L, N, and C, caused a 50 percent reduction in cell ATP. No detectable toxicity was observed with sample C after adjustment of the pH of the cell culture media, further indicating that the toxicity of this sample was due to its alkaline nature.

Textile mill samples not listed in Table 1

TABLE 1. EFFECT OF TEXTILE MILL EFFLUENTS ON RABBIT ALVEOLAR MACROPHAGE ATP AND VIABILITY

SAMPLE	ATP[*]		Viability[*]	
	EC$_{50}$ (μl/ml)	EC$_{20}$ (μl/ml)	EC$_{50}$ (μl/ml)	EC$_{20}$ (μl/ml)
T	—	25 (.02-26)	—	—
N	102 (60-197)	29 (14-50)	—	133 (61-458)
N	128 (90-188)	38 (22-56)	—	221 (129-481)
L	351 (198-849)	40 (23-63)	—	—
X	—	48 (27-80)	—	—
C[†]	335 (222-616)	61 (38-89)	—	168 (106-301)
F	—	94 (33-228)	—	—
W	—	137 (89-192)	—	—

[*] Estimated concentration (μl/ml) which should result in 50 percent and 20 percent response after 20-h exposure. The 95 percent confidence intervals are represented by numbers in parentheses.

[†] pH not adjusted before testing.

yielded such high estimates of sample concentration necessary to reduce cell viability or ATP that they could not be considered valid estimates of cytotoxicity.

Less than 10 percent of the 23 textile mill effluent samples studied measurably affected cellular viability. However, approximately 30 percent measurably affected cellular ATP in the macrophage cultures. These results indicate that measurement of cellular ATP may form a sensitive assay for evaluation of the cytotoxicity of complex environmental mixtures.

In order to further examine the cellular toxicity of the textile mill effluents, four samples evaluated in the RAM assay, including the more toxic samples (L and N), and the less toxic samples (M and R), were selected for additional studies. Figures 2 and 3 show the effect of the four samples on cellular ATP content in both the macrophage (Figure 2) and in the WI-38 human lung fibroblast (Figure 3). ATP content of macrophages and fibroblasts was depressed by samples L and N. Samples M and R were not appreciably toxic in either cell system. The similarity of response of RAM and WI 38 cells in culture has previously been reported for soluble metallic compounds (ref. 6). Such data are interesting in view of the species difference and the fact that unlike WI-38 fibroblasts, macrophages do not divide in culture. These data suggest that a variety of cell types can be used to provide an effective ranking of environmental effluents. In previous studies of the cytotoxicity of metallic salts in WI-38 and RAM cells (refs. 3,6), cellular ATP was found to be a more sensitive index of toxicity than cell viability. ATP was also a more sensitive index of toxicity of textile effluents in RAM and WI-38 cells than was cell viability. It is noteworthy that the liquid effluents from textile mills contain a variety of metallic compounds.

The measurement of cellular growth and division is one of the most widely used criteria of cellular toxicity. The CHO cell system exhibits the useful property of forming discrete colonies from single cells and, thus, can readily be used to measure cellular growth. The CHO cell system has been reported to be sensitive to a variety of environmental agents (ref. 9) including particulate materials (ref. 7). Toxicity of the textile mill effluent samples was evaluated by examination of clonal growth after a 6-day incubation period. A comparison of the dose response curves from the CHO clonal assay and ATP content in RAM and WI-38 cells after a 20-h exposure is shown in Figure 4 for cultures treated with sample N. As can be seen, clonal growth of cells was a more sensitive method for determining toxicity of sample N than assay of ATP. It was reported previously that measurement of clonal growth in CHO cells was equivalent in sensitivity to assay of ATP in the macrophage for evaluation of the toxici-

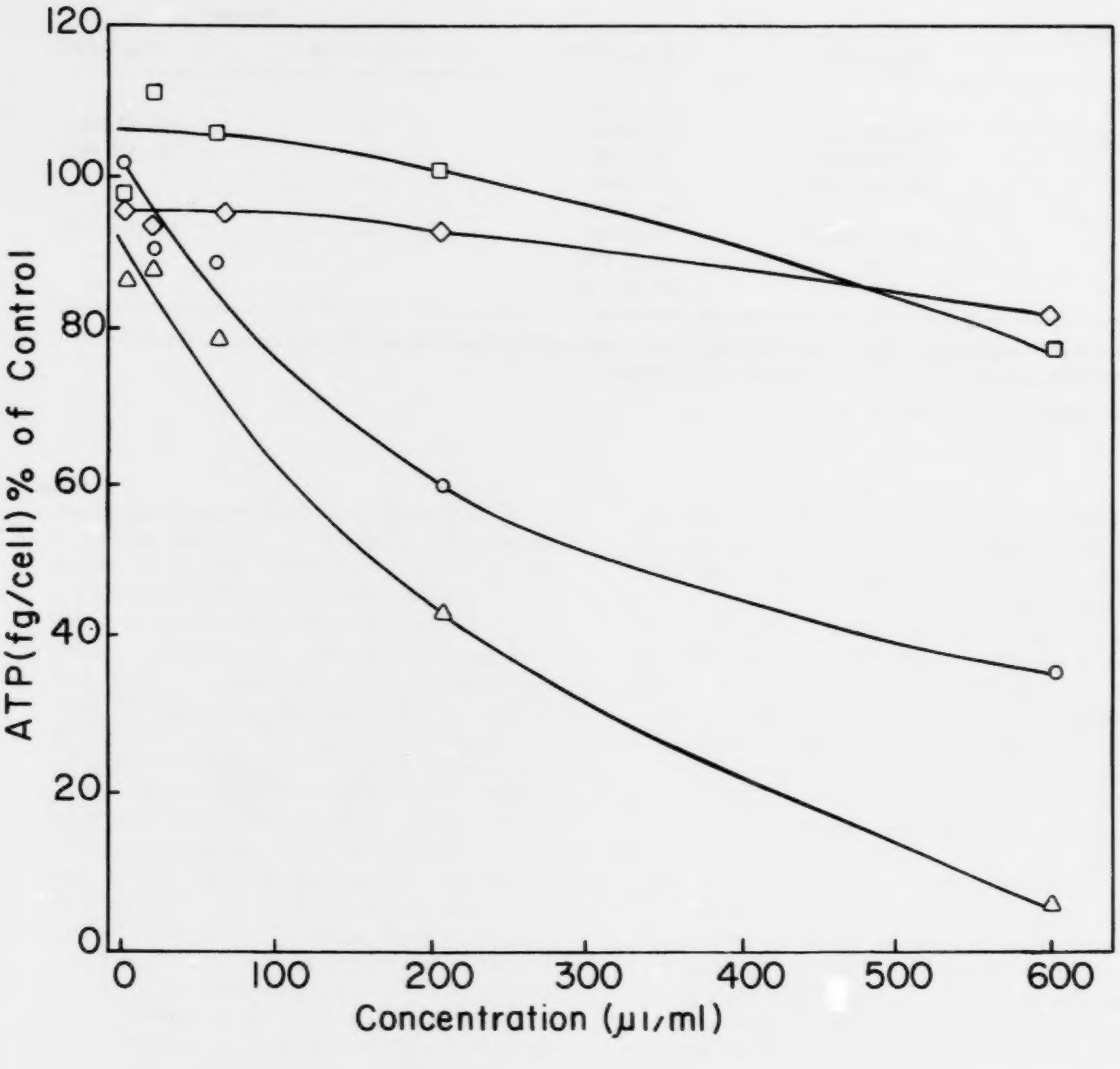


Figure 2. The effect of textile mill effluent samples M (□ – □), R (◇ – ◇), L (O – O), and N (Δ – Δ) on ATP content of the rabbit alveolar macrophage after a 20-h exposure.

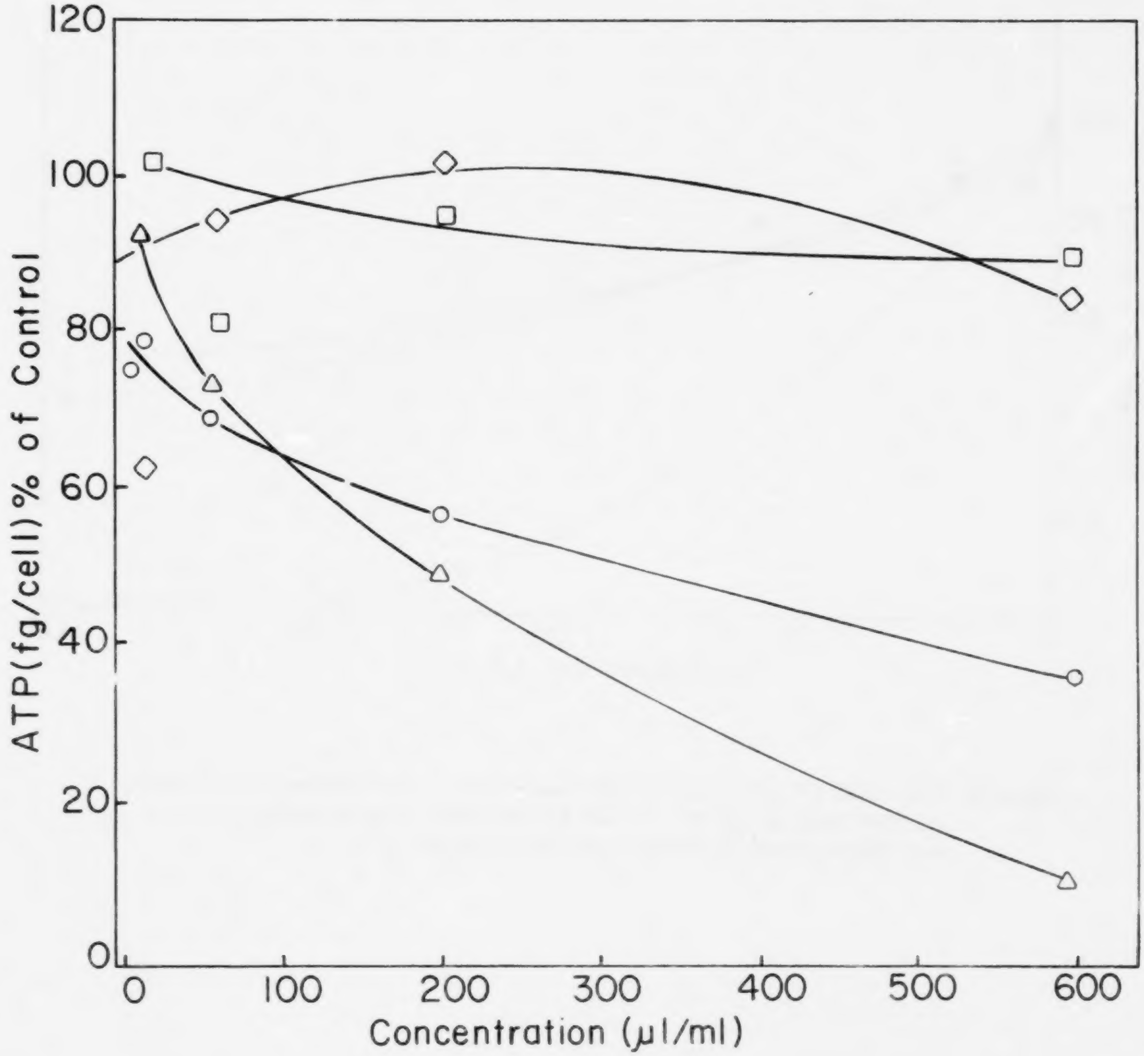


Figure 3: The effect of textile mill effluent samples M (□ – □), R (◇ – ◇), L (O – O), and N (Δ – Δ) on ATP content of the WI-38 human lung fibroblast after a 20-h exposure.

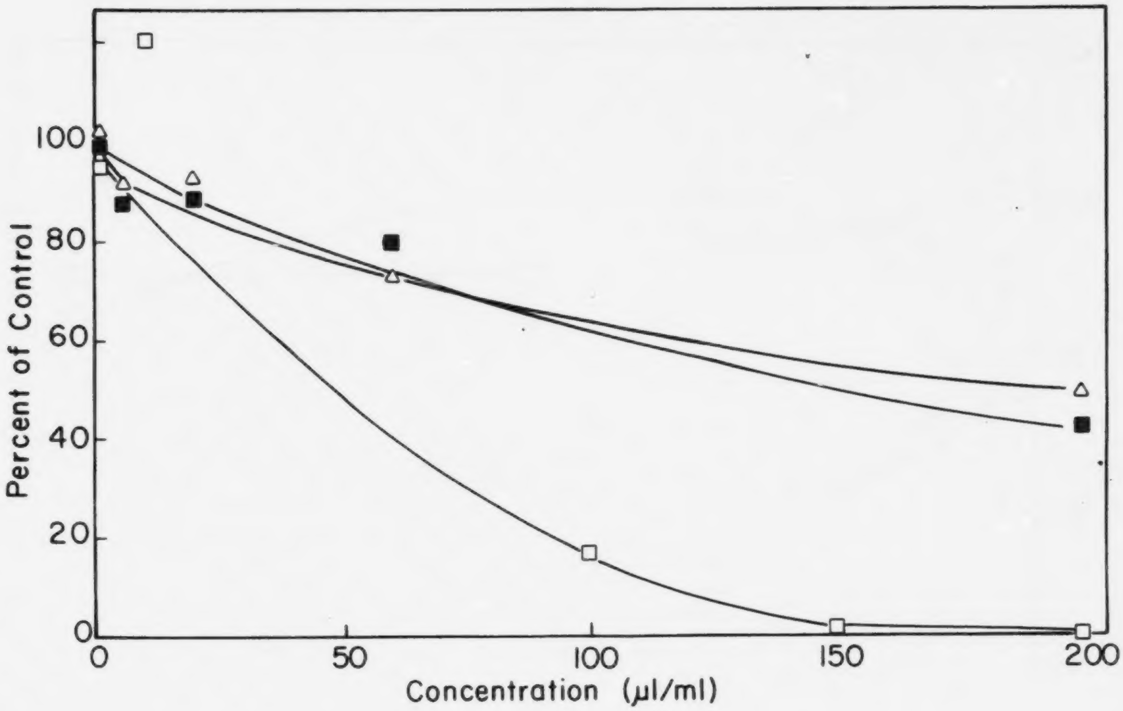


Figure 4. The effect of textile mill effluent sample N on ATP content of the rabbit alveolar macrophage (■ – ■) and WI-38 human lung fibroblast (Δ – Δ), and clonal growth in Chinese hamster ovary cells (□ – □).

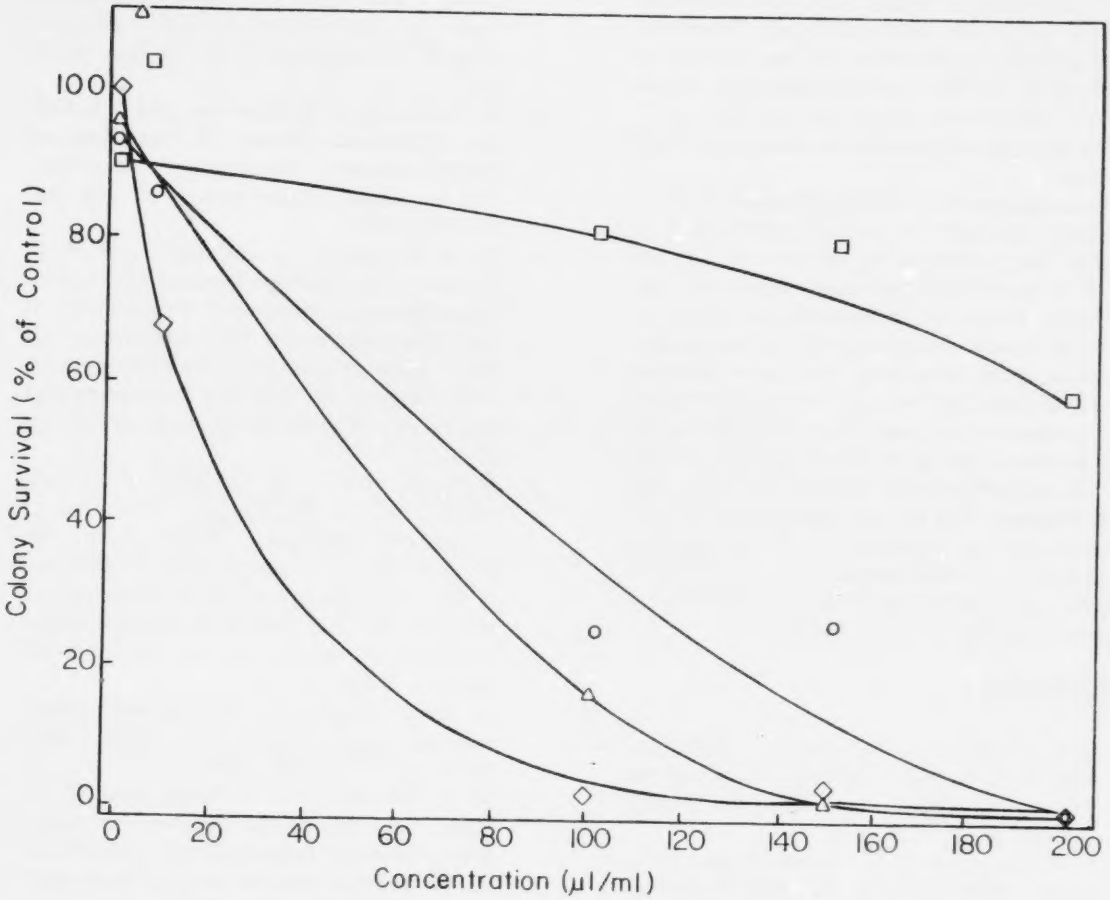


Figure 5. Colony survival after treatment of Chinese hamster ovary cells with textile mill effluent sample M (□ — □), L (O — O), N (Δ — Δ), and R (◇ — ◇). Toxicity of the samples was evaluated by counting the number of colonies formed after a 6-day exposure period.

ty of some particulate materials (ref. 7).

Figure 5 shows dose response curves for samples L, M, N, and R, which were evaluated in the CHO clonal assay. In this system, R was the most toxic of the four samples, reducing colony formation to less than 2 percent of the control value at 100 μl/ml of effluent. Samples L and N were about equally toxic, and sample M was the least toxic in the CHO test. There was no immediate explanation for the toxicity of sample R in the CHO system since this sample did not appreciably affect cell viability, ATP, or cell number when tested in RAM and WI-38 cultures.

Clonal assays may offer a different measure of relative toxicity for some environmental effluents than proliferating cultures such as the WI-38 or nondividing cultures such as the macrophage. However, in experiments aimed at the evaluation of toxicity of environmental particulates, good agreement was seen between the RAM and CHO systems when biochemical or cytochemical endpoints were utilized (ref. 7). Furthermore, the agreement seen for a number of endpoints in the WI-38 and RAM systems suggests that similar mechanisms of cytotoxicity may be operative in these systems. Questions involving comparative cytotoxicity may be resolved by additonal studies using a variety of cell systems and toxicants.

REFERENCES

1. D. L. Coffin, D. E. Gardner, R. S. Holzman, and F. J. Wolock, "Influence of Ozone on Pulmonary Cells," *Arch Environ Health*, Vol. 16, pp. 633-636, 1968.
2. D. E. Gardner, R. S. Holzman, and D. L. Coffin, "Effects of Nitrogen Dioxide on Pulmonary Cell Population," *J Bacteriol*, Vol. 98, pp. 1041-1043, 1969.
3. M. D. Waters, D. E. Gardner, C. Aranyi, and D. L. Coffin, "Metal Toxicity for Rabbit Alveolar Macrophages *in vitro*," *Environ Res*, Vol. 9, pp. 32-47, 1975.
4. M. D. Waters, T. O. Vaughan, D. J. Abernathy, H. R. Garland, C. C. Cox, and D. L. Coffin, "Toxicity of Platinum (IV) Salts for Cells of Pulmonary Origin," *Environ Health Perspectives*, Vol. 12, pp. 45-56, 1975.
5. M. D. Waters, D. E. Gardner, and D. L. Coffin, "Cytotoxic Effects of Vanadium on Rabbit Alveolar Macrophages *in vitro*," *Toxicol Appl Pharmacol*, Vol. 28, pp. 253-263, 1974.
6. M. D. Waters, J. L. Huisingh, and N. E. Garrett, "The Cellular Toxicity of Complex Environmental Mixtures," Proceedings of the Symposium on the Application of Short-Term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures, Williamsburg, VA, 1978, in press.
7. N. E. Garrett, J. A. Campbell, J. L. Huisingh, and M. D. Waters, "The Use of Short-term Bioassay Systems in the Evaluation of Environmental Particulates," Proceedings of the Symposium on the Transfer and Utilization of Particulate Control Technology, Denver, CO, July 24, 1978, in press.
8. A. Hald, "Statistical Theory with Engineering Applications," New York, John Wiley and Sons, Inc., 1952.
9. M. T. Wininger, F. A. Kulik, and W. D. Ross, "In Vitro Clonal Cytotoxicity Assay Using Chinese Hamster Ovary Cells (CHO-Kl) for Testing Environmental Chemicals," *in vitro*, Vol. 14, p. 381, 1978.

REPEATED-EXPOSURE TOXICOLOGY STUDIES

Robert J. Weir*

Abstract

In the conduct of toxicology evaluation there are acute and repeated studies on chemicals. Acute studies are useful in providing information on single-dose exposures. The results of these studies are used to compare the acute toxicity of chemicals in terms of their LD_{50}*'s, to provide labeling information, and to provide the industrial clinician with information to protect or treat workers in cases of accidental exposure.*

Repeated exposure studies are used to predict cumulative effects in man in terms of chemical exposure of a continuous or repeated nature. The data from these studies are used to explore safety and risk in intended repeated exposure (i.e., food additives, drugs) or in accidental exposure (pesticides, environmental contaminants).

Repeated exposure studies are usually carried out on the basis of two durations: subchronic (usually 90 days duration) or chronic (usually lifetime exposure—defined as 24 months in rats and mice). Dosages for chronic studies are established on the basis of results from subchronic studies.

The actual designs of repeated exposure studies vary from product to product. This results from the requirements on toxicologists in the different regulatory agencies and their own individual preferences, rather than for any rational reason. Our test animals cannot differentiate among drugs, pesticides, food additives, color additives, or environmental chemicals. Efforts are now being made to unify study designs.

Disregarding these interagency differences, an adequate 90-day subchronic study would have a minimum of four groups of test animals: one control group and three groups of test animals. The test group dosages would vary one from another on a logarithmic basis. The population of animals in each group would be no smaller than 15 males and 15 females. The test group doses would be selected so that an effect is characterized in at least one group.

Every effort should be made to establish a maximum tolerated dose for chronic studies; i.e., that dosage which produces an effect that would not be so severe as to interfere with the course of the chronic study.

Parameters measured should include: clinical observations, body weight, food consumption, hematology, blood chemistry, urine analysis, gross pathology, microscopic pathology, and survival rate.

An adequate chronic study would have a minimum of four groups of test animals, one of which is a control group. The high-dosage group would receive a maximum-tolerated dose. The middle-dose group would receive half the maximum-tolerated dose. The low dose would have a relationship to the level expected in the environment. Each control and test group should contain a minimum of 50 male and 50 female animals, if rats or mice are used as test subjects.

The parameters measured should be the same as those in the subchronic study. Since the chronic study can also be an oncogenesis (cancer) study, emphasis should be placed on the tissue masses during observation of signs of toxicity and at gross necropsy. Microscopic examination should be made on approximately 40 major tissues from each animal. The tissues should be read from all animals in the control and high-level dose groups, showing reduced survival, and/or the highest group, showing no reduced survival. Target organs should be examined in all low-level group animals.

Let us turn our attention to textile chemicals, biological assessment, and the Toxic Substances Control Act (TOSCA). If textile chemicals are found to have biological activity in

---

*Vice President, Litton Bionetics, Inc., Kensington, MD.

EPA's Level 1 Environmental Assessment or when they are studied under TOSCA, they will be examined according to the above or similar protocols.

It is extremely important that the material of commerce associated with activity in Level 1 Environmental Assessment and studies in toxicological experiments be characterized chemically. It is possible that the material manufactured may not be identical to that found in the environment. Special chemical synthesis and toxicological evaluation may be required under these circumstances.

If one eliminated the question of carcinogenesis then, almost without exception, the results of chronic studies could be predicted from the results of the subchronic or 90-day studies (ref. 1). The question of carcinogenesis could be predicted on the basis of the Ames Test, mouse lymphoma, or malignant transformation studies with a correlation factor above 90 percent. The textile manufacturer, but not the regulatory agency, can be well assured on the basis of these two studies that the material is or is not a problem without conducting the chronic study. With further research it may eventually be possible to improve the correlation of predictive short-term studies so that regulatory agencies will be able to accept this philosophy and reduce time and costs as well.

REFERENCES

1. M. A. Mehlman, R. Shapiro, and H. Blumenthal, *Advances in Modern Toxicology - New Concepts in Safety Evaluation,* Vol. 1, Part 1, Chapter 4, Hemisphere Publ. Corp., Washington, DC, 1976.

ASSESSMENT OF TEXTILE WASTE TOXICITY WITH MARINE BIOASSAYS*

Gerald E. Walsh, Lowell H. Bahner[†]

Abstract

Marine bioassays were conducted with textile wastes on an alga (Skeletonema costatum), *the grass shrimp* (Palaemonetes pugio), *and the sheepshead minnow* (Cyprinodon variegatus). *Effects measured were inhibition or stimulation of algal growth and death of animals after 96-h exposure.*

All wastes affected growth of S. costatum, *whereas only five were acutely toxic to the animals. Grass shrimp were more sensitive than juvenile sheepshead minnows: the range of the LC50 was 12.8 to 34.5 percent waste for the shrimp compared to 37.5 to 69.5 percent for the minnow. Four wastes stimulated growth of algae (SC20 = 0.50 to 2.25 percent); four inhibited growth (EC50 = 1.5 to 84 percent); six were both stimulatory at low concentrations (SC20 = 1.5 to 21.75 percent) and inhibitory at high concentrations (EC50 = 50 to 93 percent). The SC20, a term introduced here, is the calculated concentration of waste that would stimulate growth by 20 percent above the control.*

Algae must be considered very useful for assessment of possible effects of textile wastes on aquatic systems because they responded to all wastes tested.

It is suggested that bioassays be used to assess the potential impact of whole waste on aquatic systems; and after chemical analysis of the waste, bioassays be performed on components that may be bioactive. If the whole waste or any of its components has an effect, then that waste must be considered for application of treatment technology.

INTRODUCTION

Population growth and the rate of industrial development along coastlines in the United States have been accelerating within recent years, and acceleration is expected to continue in the forseeable future. In 1972 the U.S. Department of Commerce (ref. 1) predicted that the total human population density around 39 cities on the Atlantic, Pacific, and Gulf Coasts, and in Hawaii would double between the years 1975 and 2020 (Figure 1). Concomitantly, total manufacturing around and in those cities was predicted to rise approximately 5.5 times and textile products, approximately 4.5 times.

The possible ecological impact of such growth upon estuarine and marine ecosystems is great because industrial plants often emit large volumes of effluents that contain bioactive organic and inorganic substances. Also, because the population of coastal areas will increase, the volume of sewage and municipal wastes discharged will increase, thus placing a double pollution burden upon estuarine and marine ecosystems.

Since estuaries are important commercial, recreational, and aesthetic resources, it is important to know effects of wastes upon them and to apply the proper treatment systems. This paper discusses use of bioassays to evaluate potential impacts of textile industry wastes on estuarine biota. The tests were designed to screen many wastes in a short period of time and to rank their toxicities according to effects on algae, shrimp, and fish. More sophisticated bioassays are required under stringently controlled conditions and with statistical analyses to define toxicity more precisely. Such tests will be done in IERL-RTP Level 2 bioassays.

The simplest, most direct, and inexpensive method for testing effects of complex industrial wastes upon estuarine organisms is through exposure to waste in static tests. In the work reported here, three species representative of three major classes of estuarine organisms were used:

1. *Skeletonema costatum,* a chain-forming diatom that occurs in inshore and open-ocean waters, is an algal species that has been sensitive to a variety of pollutants in our laboratory;

---

*Contribution No. 376 from the Environmental Research Laboratory, Gulf Breeze, FL.

[†] U.S. Environmental Protection Agency, Environmental Research Laboratory, Gulf Breeze, FL.

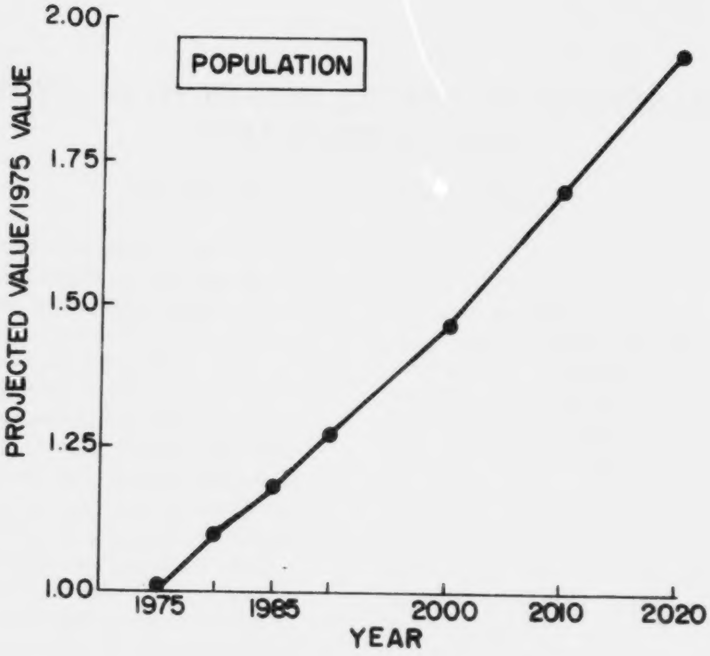


Figure 1. Projected population growth in 39 coastal cities, with 1975 as the base year.

Source: U.S. Department of Commerce (1972).

2. *Palaemonetes pugio*, the grass shrimp, is an arthropod that occupies a broad geographical range along the Atlantic and Gulf Coasts and is easy to maintain in the laboratory; and
3. Juveniles of *Cyprinodon variegatus*, the sheepshead minnow, were used because juvenile fish are often more sensitive to pollutants than adults and because *C. variegatus* is common on the Atlantic and Gulf coasts.

Since industrial wastes often contain materials that are toxic to algae and animals, and nutrients that stimulate algal growth, laboratory results must be interpreted in relation to death of animals, inhibition of algal growth, and stimulation of algal growth with the possible establishment of eutrophic conditions. A waste that has any of these effects in laboratory tests may affect an estuarine ecosystem by changing relative numbers and kinds of species, creating an assemblage of organisms that reduces its resource value.

In this paper, we identify and rank those textile plant wastes that would be likely to cause undesirable changes in estuarine ecosystems.

METHODS

Grab samples of wastes were distributed under ice in glass containers by an IERL-RTP contractor who also assigned code letters. Each species was tested with 14 wastes. *Skeletonema costatum* was tested with Wastes B, C, F, G, K, L, N, P, S, T, U, V, W, and X; *P. pugio* and *C. variegatus* were tested with A, B, C, E, F, G, K, L, N, S, T, U, W, and X. Details of methods used are described in the U.S. Environmental Protection Agency publication, *IERL-RTP Procedures Manual: Level 1* (ref. 2). A general overview of the methods is given here.

Algae

Stocks of *S. costatum* were maintained in an

TABLE 1. COMPOSITION OF MIXES ADDED TO ALGAL GROWTH MEDIA

Nutrient mixes	Amount/liter
Metal mix[‡]	
$FeCl_2 \times 6H_2O$	0.480 g
$MnCl_2 \times 4H_2O$	0.144 g
$ZnSO_4 \times 7H_2O$	0.045 g
$CuSO_4 \times 5H_2O$	0.157 mg
$CoCl_2 \times 6H_2O$	0.404 mg
H_3BO_3	0.140 g
Deionized water	1 liter
Vitamin mix[§]	
Thiamin hydrochloride	50 mg
Biotin	0.01 mg
B_{12}	0.10 mg
Deionized water	100 ml
Minor salt mix[¶]	
K_3PO_4	3.0 g
$NaNO_3$	50.0 g
$Na_2SiO_3 \times 9H_2O$	20.0 g
Deionized water	1 liter

[‡] Add 15.0 ml/l to test solution.

[§] Add 0.50 ml/l to test solution.

[¶] Add 1.0 ml/l to test solution.

artificial seawater medium (Rila® Salts[#]) of 30 parts per thousand (ppt) salinity fortified with metals, vitamins, and minor salts in deionized water (Table 1). Stocks were illuminated by "cool white" fluorescent tubes at approximately 4,000 lux in a cycle of 14 hours of light followed by 10 hours of darkness. The temperature was 20.0 ± 1.0° C.

In algal tests, artificial seawater was prepared with untreated liquid waste and diluted with artificial seawater prepared with deionized water. Added concentrations of metals, vitamins, and salts (Table 1) supported approximately one-half the final population density of full-strength growth medium. By using the concentrations and omitting a chelator from the medium, stimulation and inhibition of growth could be detected at the test pH of 8.1.

Growth tests were performed in sterile, calibrated test tubes (25 × 200 mm, Bellco Glass Co., Vineland, NJ). Twenty-five milliliters of each waste dilution were added to each of three tubes; control tubes contained the same volume of growth medium prepared with deionized water. One milliliter of algal suspension containing approximately 1,000 cells/ml was added to each tube. Similar tubes were not inoculated with algae to serve as optical blanks. All tubes were incubated on a rotary shaker at 60 excursions/min, 20 ± 0.5° C, and 4,000 lux. The lighting cycle was 14 hours light: 10 hours darkness.

After incubation for 96 hours, the absorbance of each culture was measured spectrophotometrically at 525 nm on a Fisher Electrophotometer II® (Fisher Scientific Co., Pitts-

---

[#] Rila® Products, Teaneck, NJ. Reference to trade names in this publication does not constitute endorsement by the U.S. Environmental Protection Agency.

burgh, PA). The absorbance values of uninoculated blank tubes were subtracted from those of the inoculated tubes to give the absorbance due to algae. Optical density is closely related to biomass (Walsh, unpublished), and this method was used for both range-finding and definitive tests.

Stimulation or inhibition of algal growth was calculated by plotting the nonlinear regression of absorbance on waste concentration by an equation developed for these studies:

$$Y = \frac{A}{1 + B\,(X - C)} - \frac{A}{1 + D\,(X - E)}$$

where

A = mean maximum biomass
B = increasing slope
C = effluent concentration (increasing slope) where $Y = 0.5 \times A$
D = decreasing slope
E = effluent concentration (decreasing slope) where $Y = 0.5 \times A$
X = range of effluent concentrations tested
Y = estimated population density over range of X.

Calculations were made on a Digital Equipment Corporation PDP 11/45 computer. The concentration of waste that stimulated growth by 20 percent (SC20) or inhibited growth by 50 percent (EC50) in relation to control cultures was calculated from the regression curve.

Shrimp and Fish

Palaemonetes pugio and *C. variegatus* juveniles were collected from the field and held in flowing water for at least 2 days while being acclimated to a salinity of 10 ppt. Each test was performed in 3 liters of test solution in 4-liter glass jars. Five animals were tested per jar and all exposures were done in duplicate in definitive tests. The jars were not aerated, but oxygen content was measured each day by the Winkler method. Temperature was 20 ± 1.0°C.

Salinity of the effluents was increased by 10 ppt by addition of Rila® Salts. Control and dilution water were prepared from Rila® Salts and glass-distilled water.

Each effluent was subjected to a 48-h range-finding test. If no deaths occurred in undiluted waste, the exposure was continued to 96 hours. If mortality was equal to or less than 50 percent after 96 hours, no further tests were done. If mortality was greater than 50 percent, 96-h definitive tests were done.

Concentrations of wastes that would kill 50 percent of the animals in 96 hours (LC50) were calculated by straight-line graphical interpolation. Points representing the number of deaths in concentrations lethal to more than one-half and less than one-half of the animals exposed were plotted on semilogarithmic coordinate paper. The concentration at which a straight line drawn between two points crossed the 50 percent mortality line was the estimated LC50.

RESULTS

Algae

Skeletonema costatum was a valuable organism for detection of possible impacts of textile industry wastes on natural waters. All of the 14 wastes tested affected growth; 4 were inhibitory only, 4 were stimulatory only, but 6 were stimulatory at low concentrations and inhibitory at high concentrations (Table 2).

The patterns of growth response in relation to waste concentrations are given in Figures 2 to 16. Wastes B, S, U, and X were stimulatory only; Wastes F, L, N, and P were inhibitory only; and Wastes C, G, K, T, V, and W were both stimulatory and inhibitory. When inhibition and stimulation occurred, the SC20 was much lower than the EC50.

Shrimp

Only 5 of the 14 textile effluents caused greater than 50 percent mortality of *P. pugio* in concentrations up to 100 percent (Table 2). The most toxic was Waste C (LC50 = 12.8 percent), followed by Wastes W (19.6 percent), A (21.2 percent), N (26.3 percent), and T (34.5 percent). Three effluents caused mortality of less than 50 percent and no LC50 could be calculated. The six remaining wastes (B, F, K, L, U, and X) caused no deaths when grass shrimp were exposed to 100 percent effluent for 96 hours.

The percentage of oxygen saturation of the test solutions was never lower than 40. Therefore, deaths were due directly to the wastes and not to oxygen deficiency. There was no mortality in the controls.

TABLE 2. COMPARISON OF RESPONSE OF SKELETONEMA COSTATUM, PALAEMONETES PUGIO, AND CYPRINODON VARIEGATUS TO TEXTILE WASTES

Waste	S. costatum		P. pugio	C. variegatus
	SC20	EC50	LC50	LC50
C	1.50	76	12.8	69.5
N	NE	2.0	26.3	47.5
T	2.00	66	34.5	68.0
W	1.50	50	19.6	37.5
A	–	–	21.2	62.0
B	0.50	NE	NE	NE
F	NE	84	NE	NE
G	2.75	59	*	†
K	1.00	75	NE	NE
L	NE	1.5	NE	‡
S	2.25	NE	*	*
U	1.50	NE	NE	NE
V	21.75	93	NE	NE
x	0.50	NE	NE	NE
E	–	–	†	
P	NE	9.0	–	–

*20 percent mortality in 100 percent waste
†40 percent motality in 100 percent waste
‡50 percent mortality in 100 percent waste
§10 percent mortality in 100 percent waste

Notes: SC20 = percentage waste at which growth was stimulated by 20 percent;
EC50 = percentage waste at which growth was inhibited by 50 percent;
LC50 = percentage waste lethal to 50 percent of the animals;
NE = no effect.

Fish

Acute toxicities of the 14 textile effluents to juvenile sheepshead minnows are shown in Table 2. Only five wastes were toxic enough to allow calculation of the LC50 (Waste W, 37.5 percent; N, 47.5 percent; A, 62.0 percent; T, 68.0 percent; and C, 69.5 percent). Mortalities in Wastes E, G, L, and S were not great enough to calculate LC50 values, and Wastes E, F, K, U, and X had no effect on survival in 96 hours.

As in the shrimp tests, percentage saturation of oxygen in test solutions was never lower than 40, so deaths were not due to lack of oxygen. There was no mortality in the controls.

DISCUSSION

The alga *S. costatum* was the most sensitive organism in these tests: all wastes affected growth of the alga, whereas only five were acutely toxic to *P. pugio* and *C. variegatus*. Table 2 contrasts responses of the three organisms to the wastes. These results were unexpected, since animals are usually more susceptible to single pollutants than algae, and it seems that algae are better indicators of effects of some complex wastes than are animals. Also, the stimulatory effects of some wastes on algae indicate that industrial wastes may have a greater effect in bringing about eutrophication than previously realized.

Palaemonetes pugio was more sensitive to the wastes than *C. variegatus*, but neither was of value for ranking of all wastes because toxicity was detected in only five effluents. As shown in Table 3 the two species also responded differently.

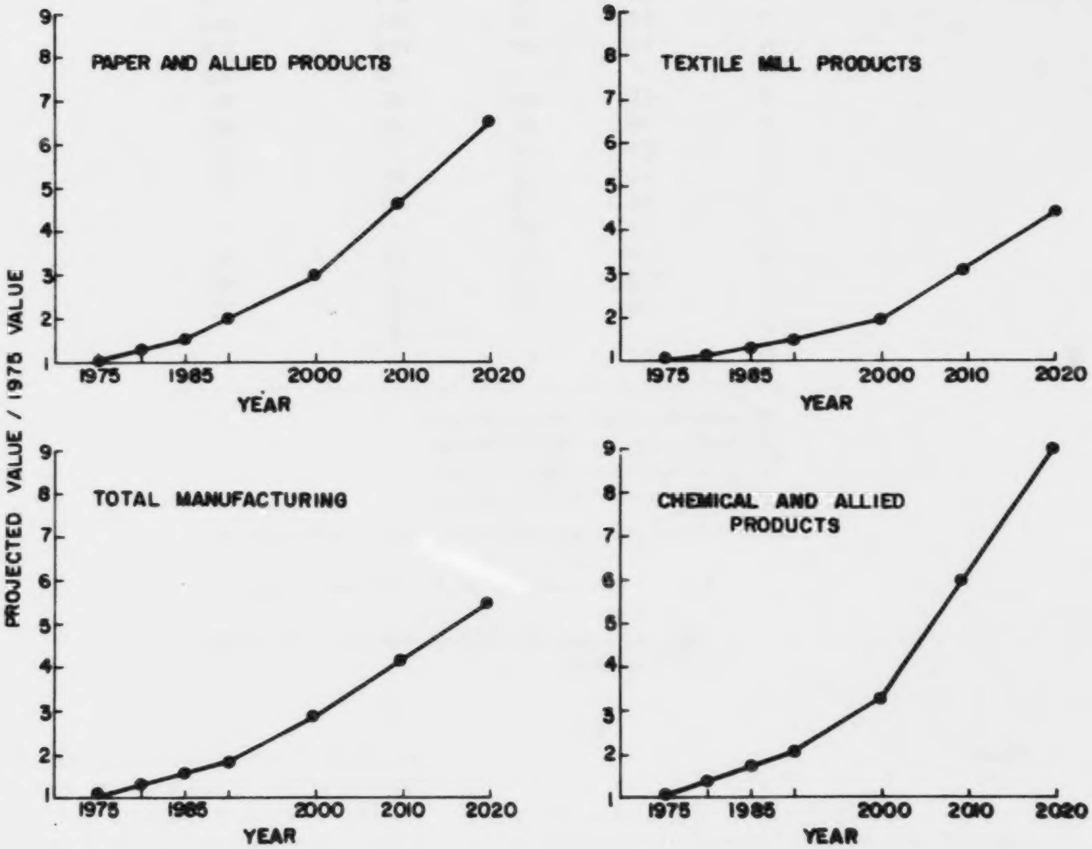


Figure 2. Projected industrial growth in 39 coastal cities, with 1975 as the base year.

Source: U.S. Department of Commerce (1972).

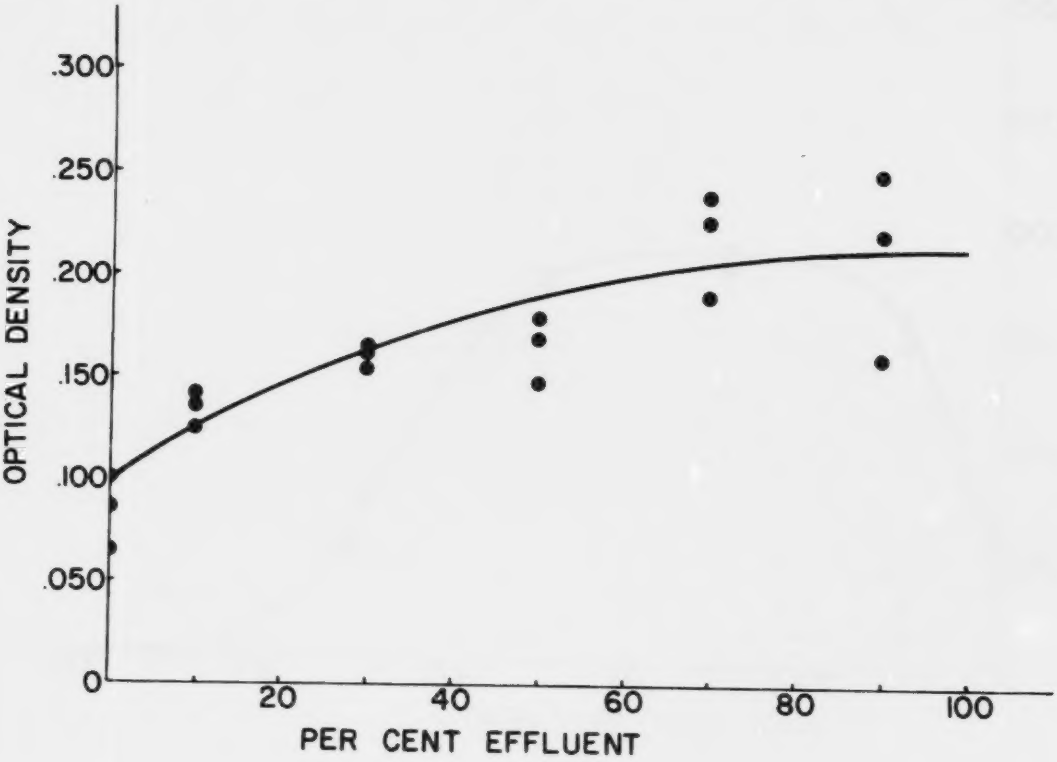


Figure 3. Effects of Textile B effluent on growth of *Skeletonema costatum*.

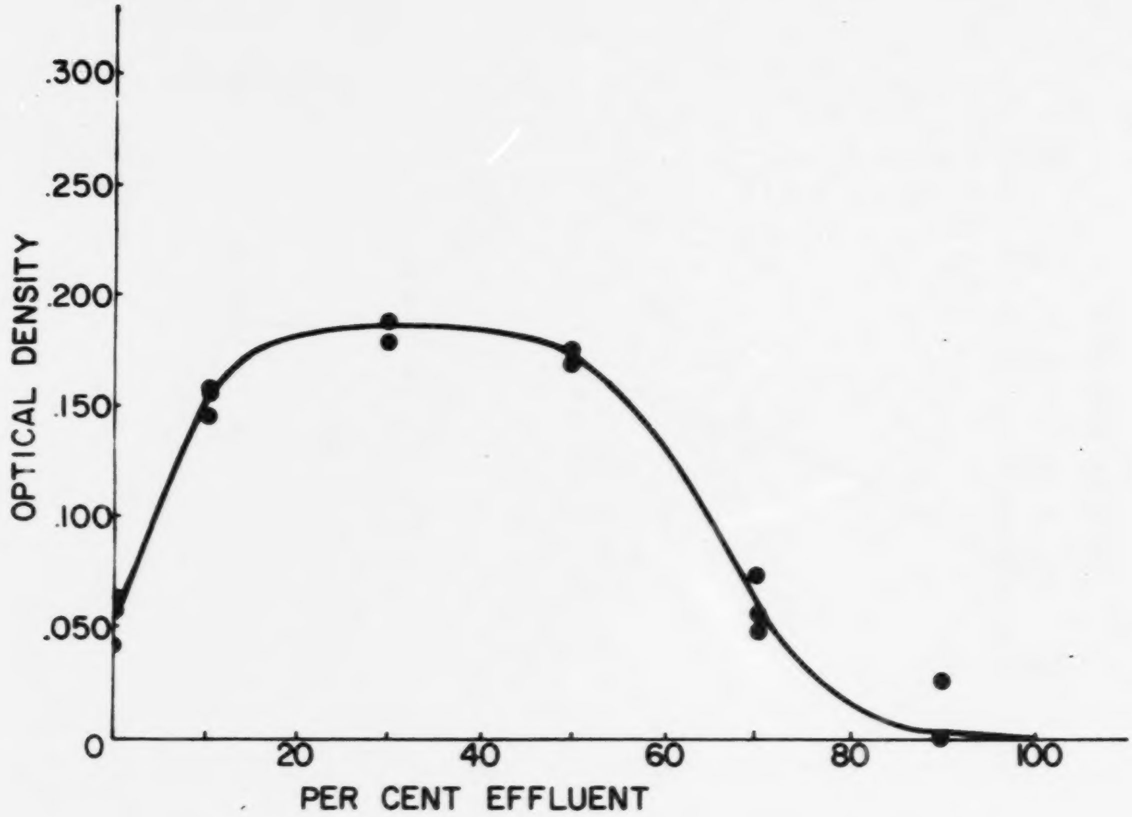


Figure 4. Effects of Textile C effluent on growth of *Skeletonema costatum.*

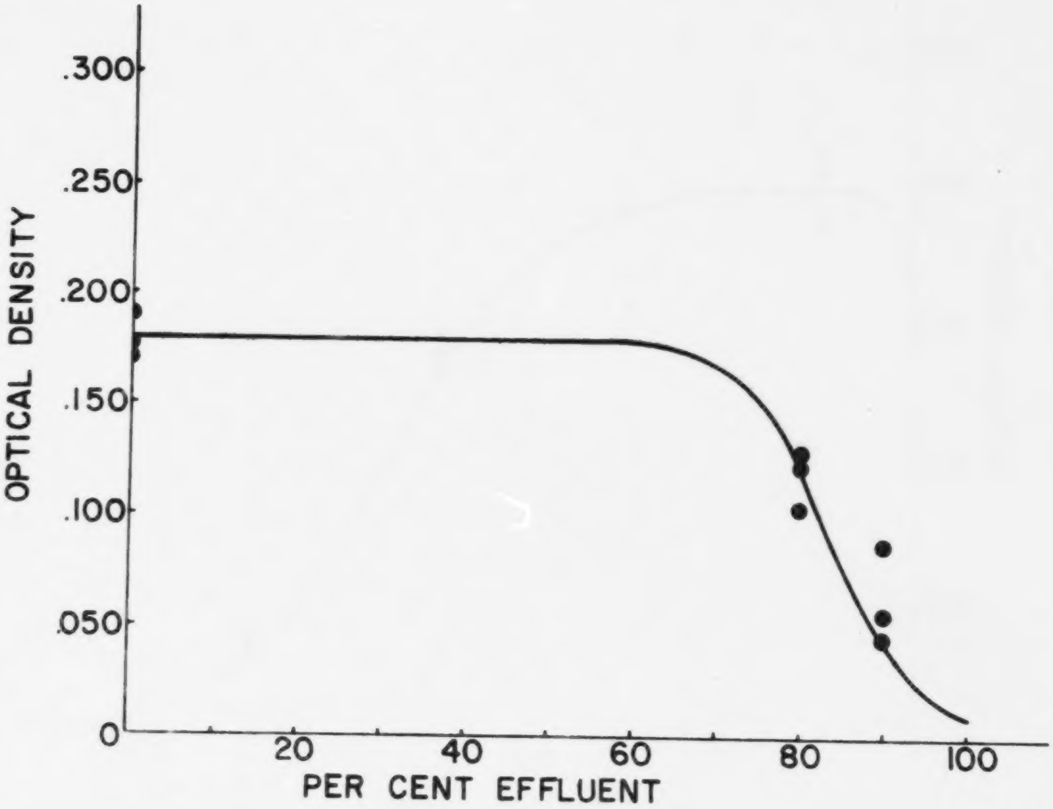


Figure 5. Effects of Textile F effluent on growth of *Skeletonema costatum.*

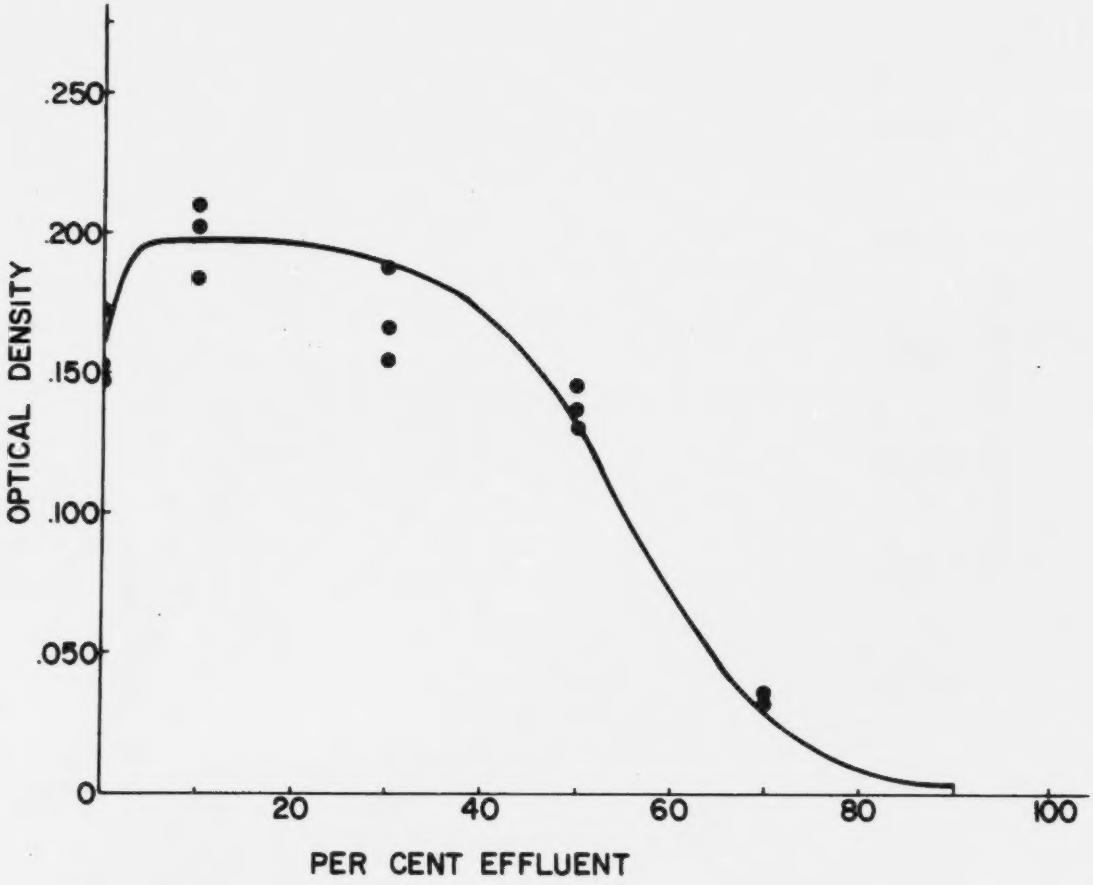


Figure 6. Effects of Textile G effluent on growth of *Skeletonema costatum.*

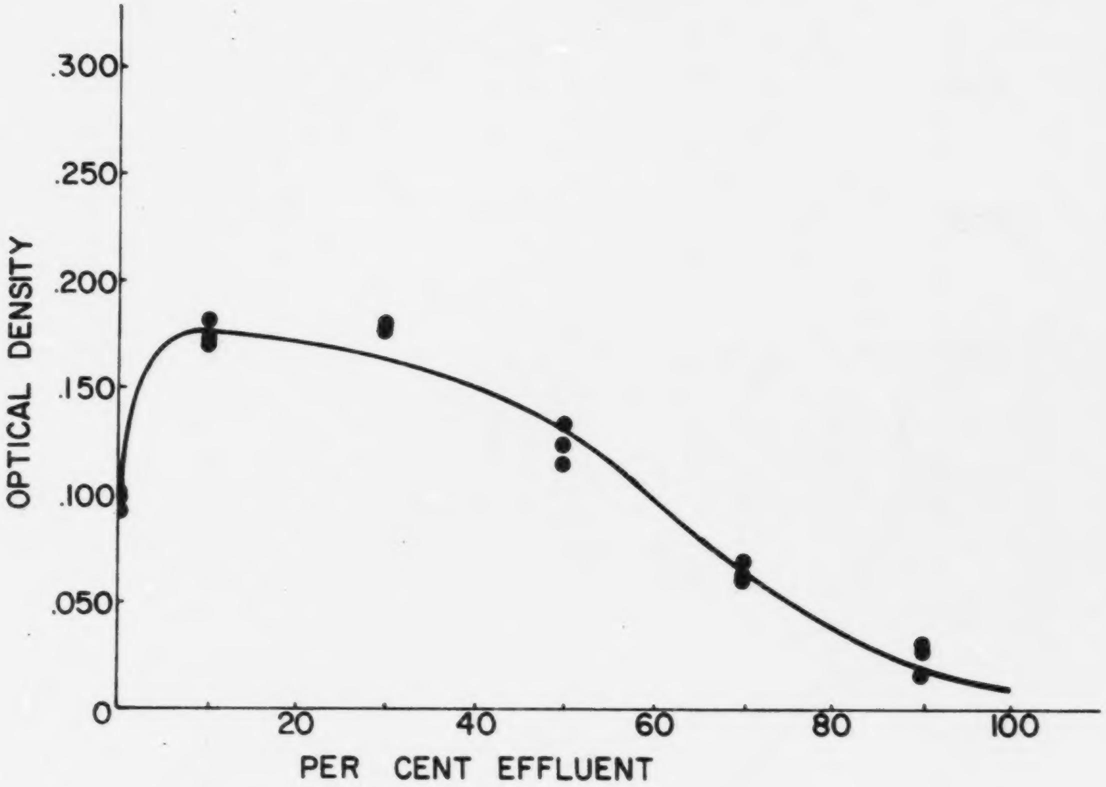


Figure 7. Effects of Textile K effluent on growth of *Skeletonema costatum.*

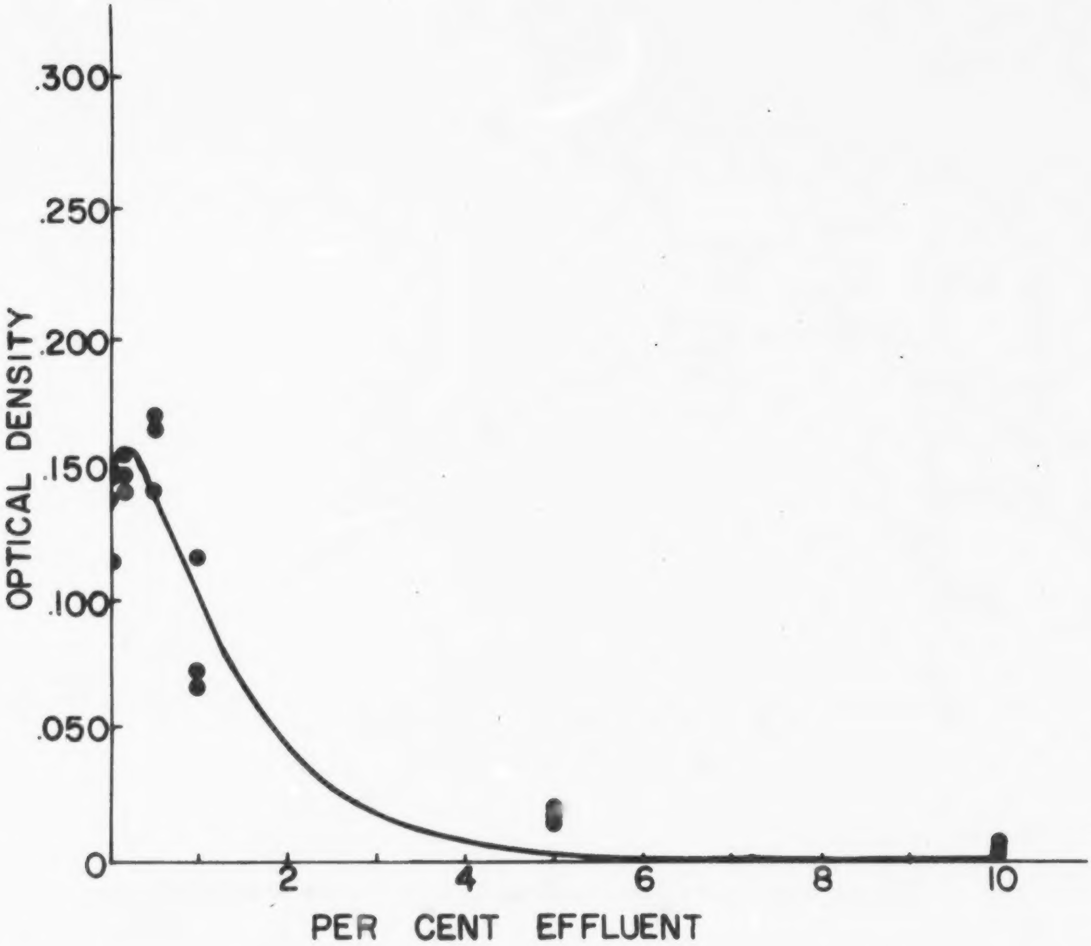


Figure 8. Effects of Textile L effluent on growth of *Skeletonema costatum*.

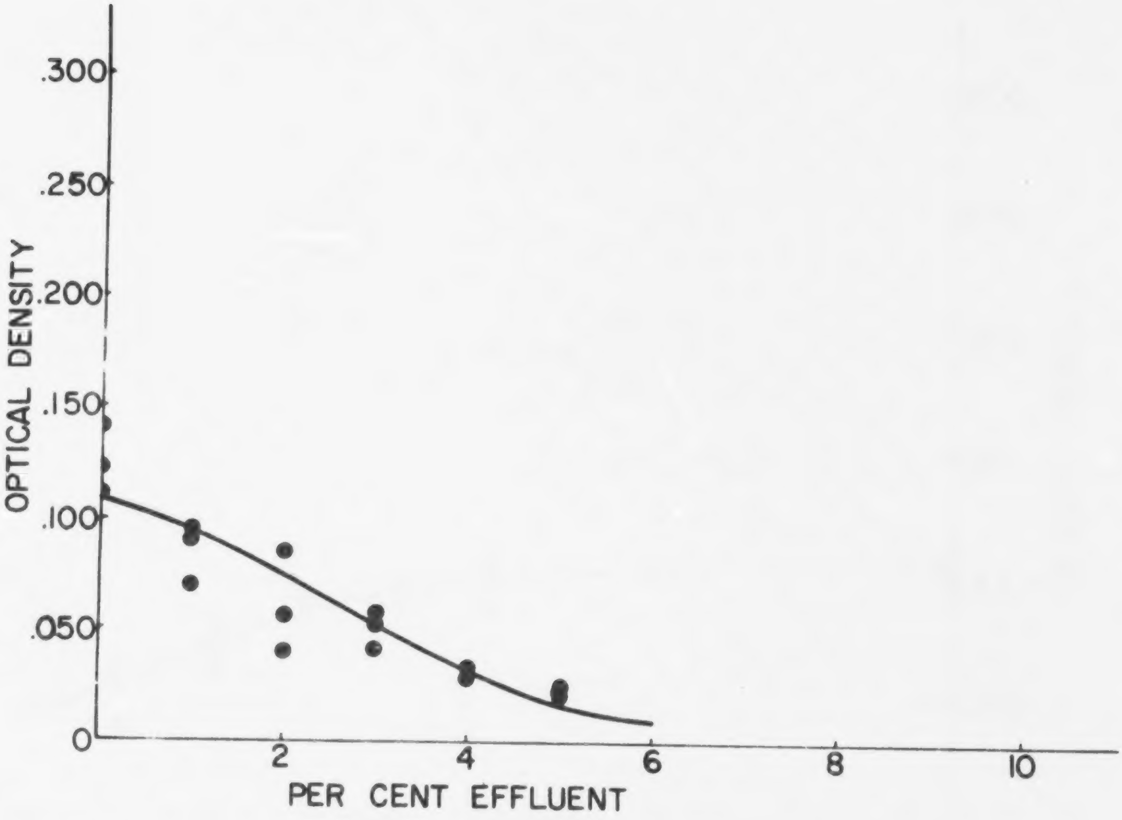


Figure 9. Effects of Textile N effluent on growth of *Skeletonema costatum.*

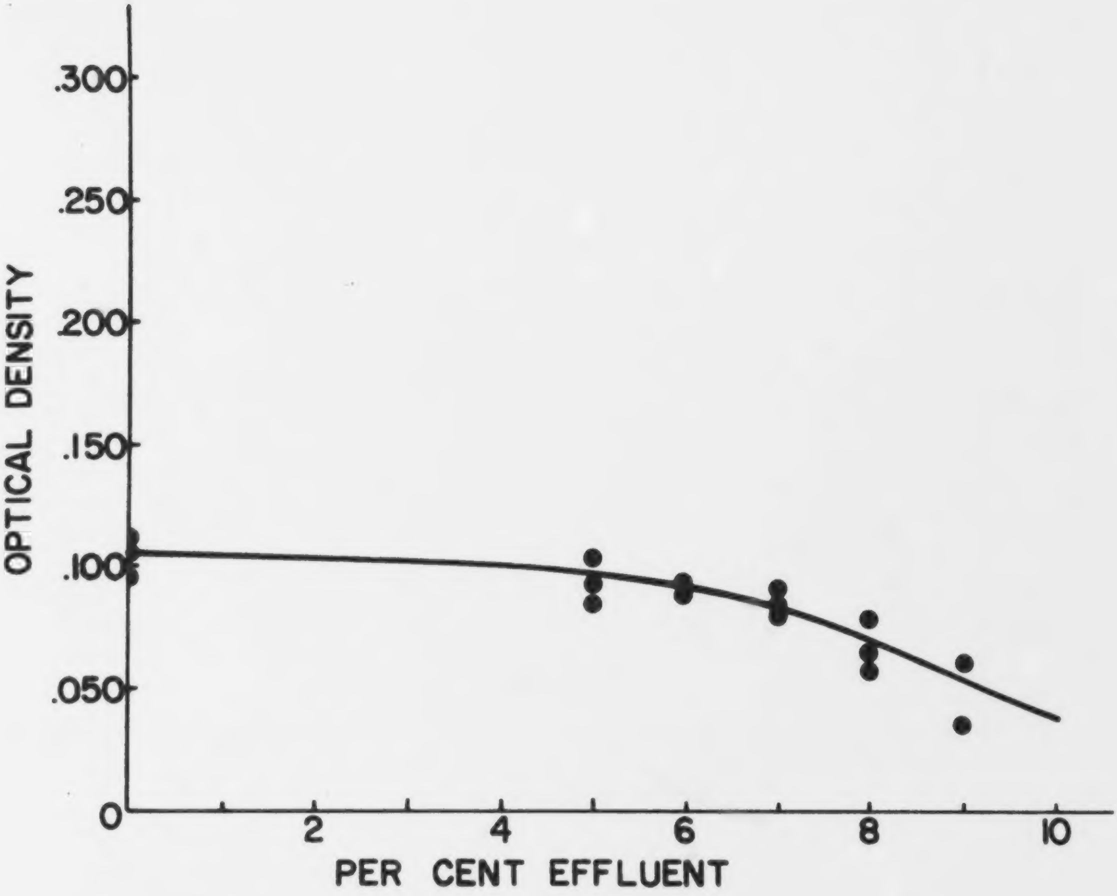


Figure 10. Effects of Textile P effluent on growth of Skeletonema costatum.

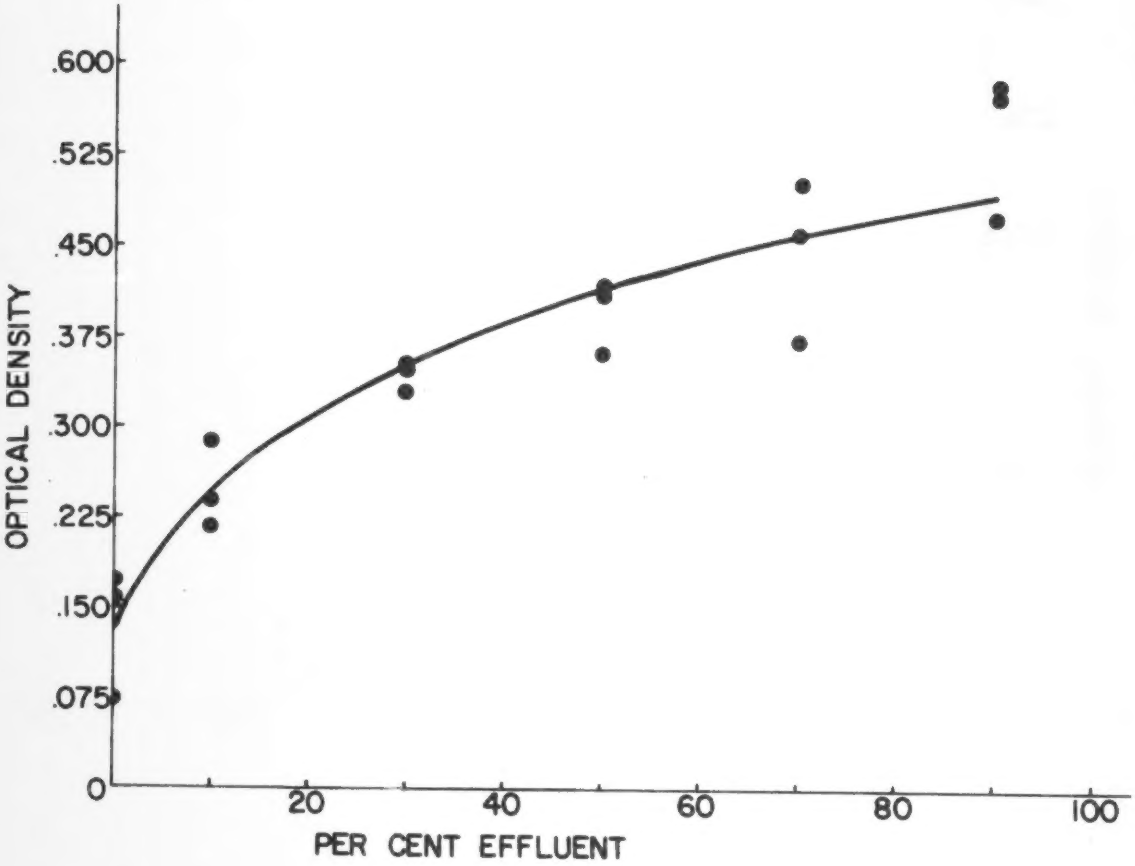


Figure 11. Effects of Textile S effluent on growth of *Skeletonema costatum*.

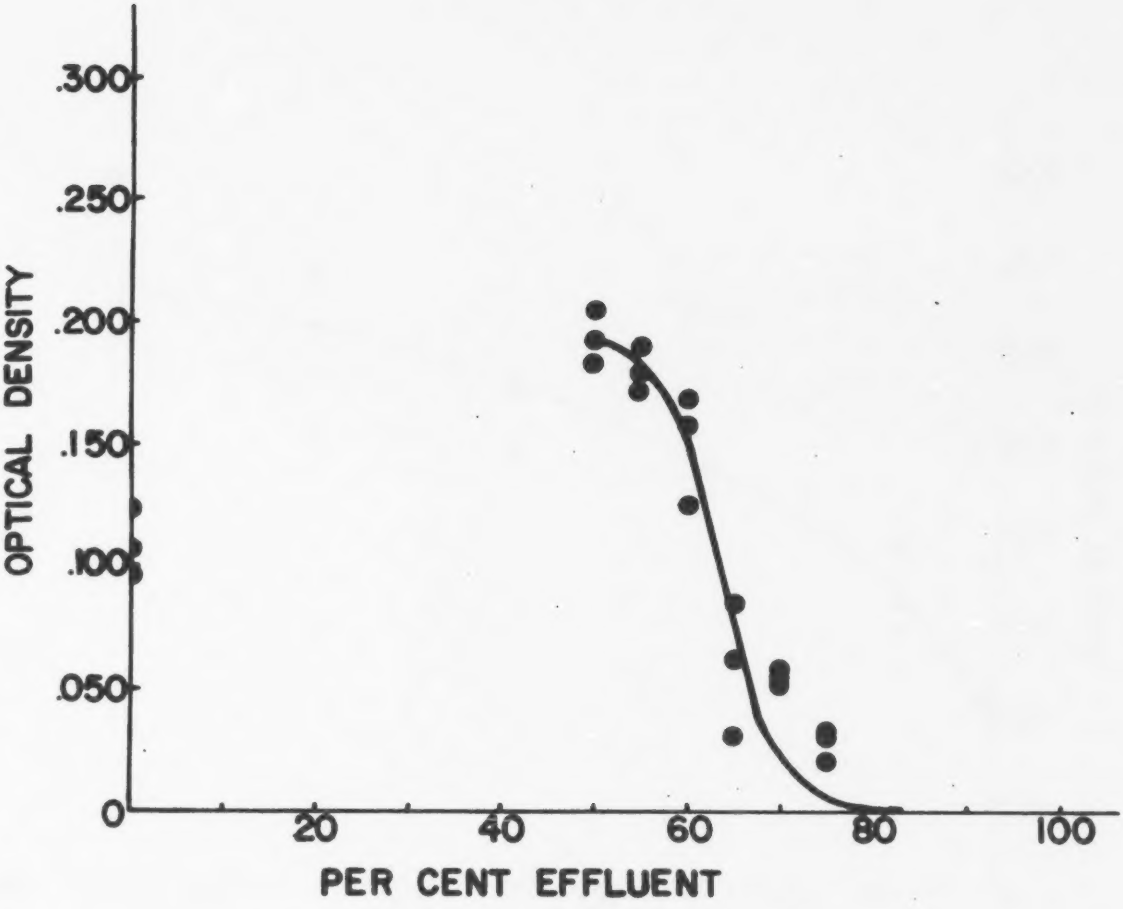


Figure 12. Effects of Textile T effluent on growth of Sketonema costatum.

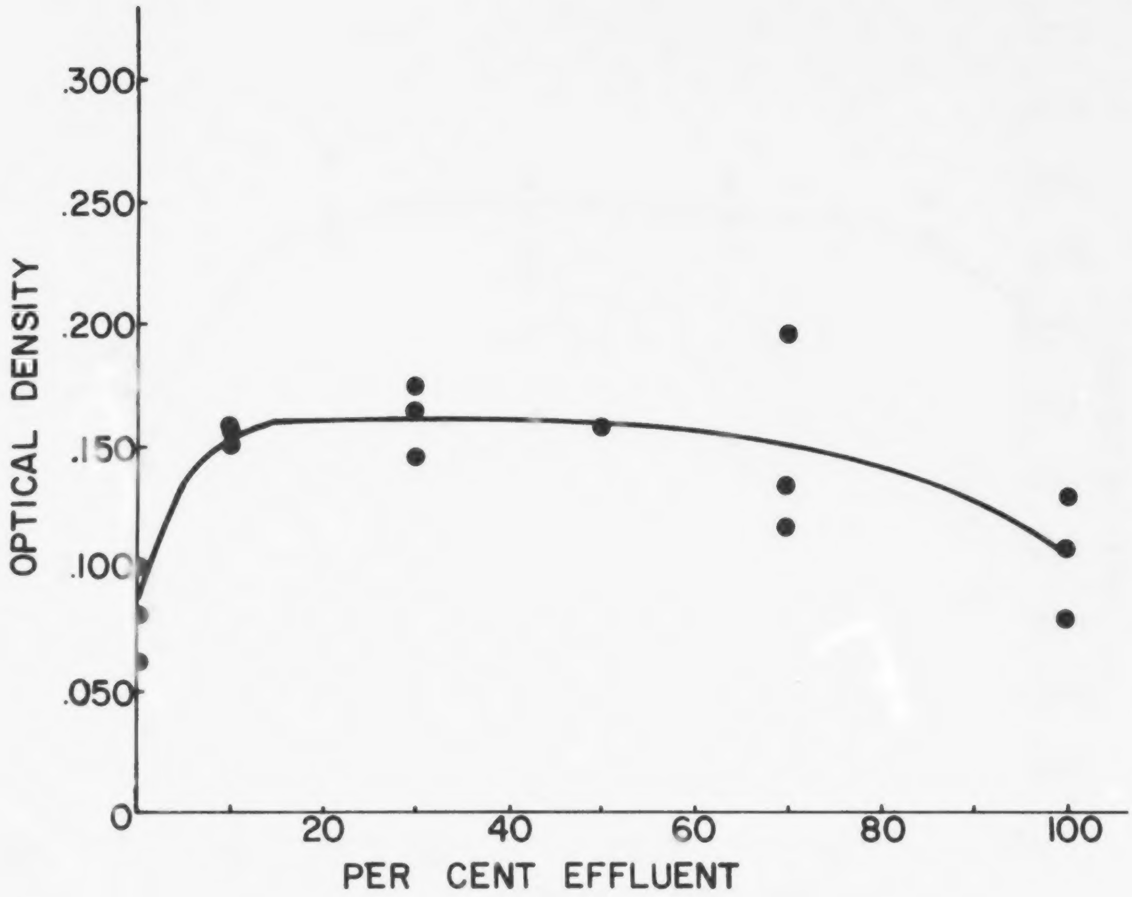


Figure 13. Effects of Textile U effluent on growth of Skeletonema costatum.

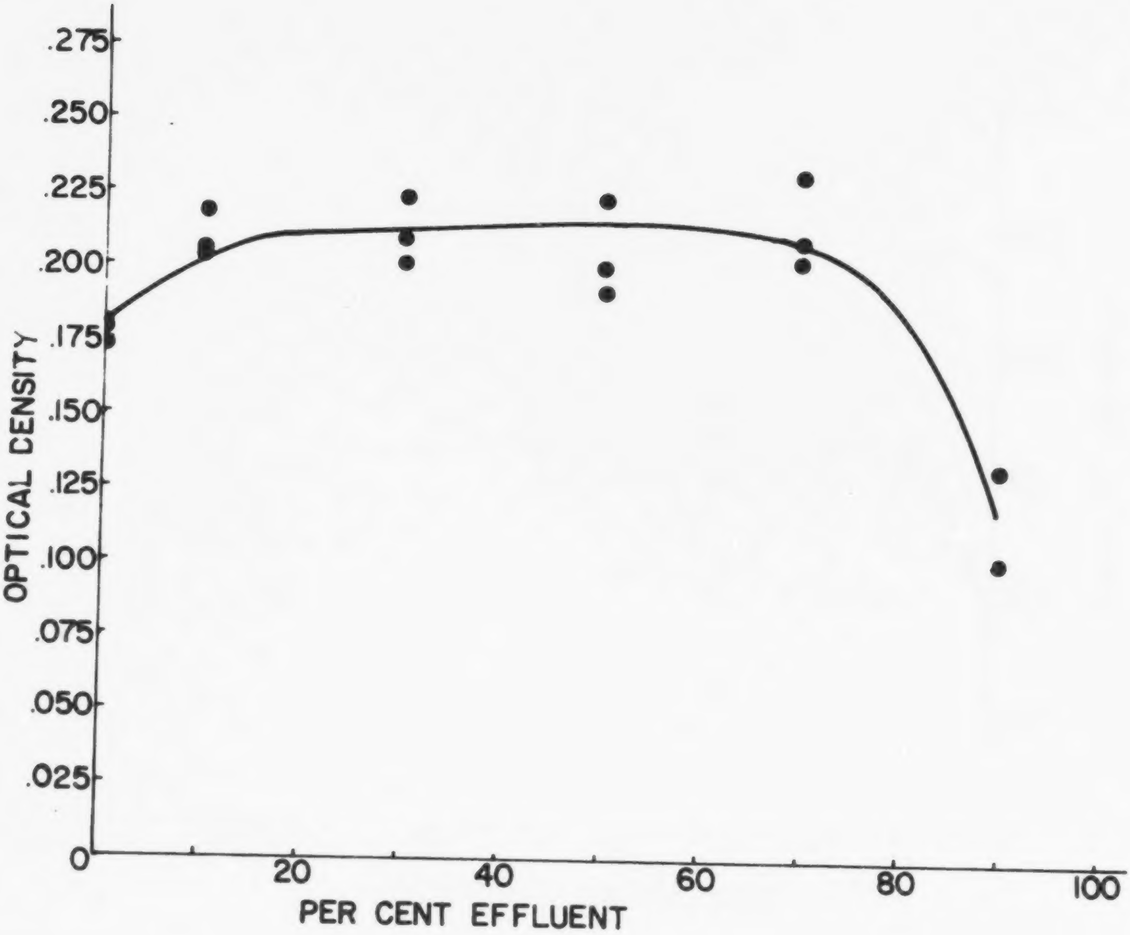


Figure 14. Effects of Textile V effluent on growth of Skeletonema costatum.

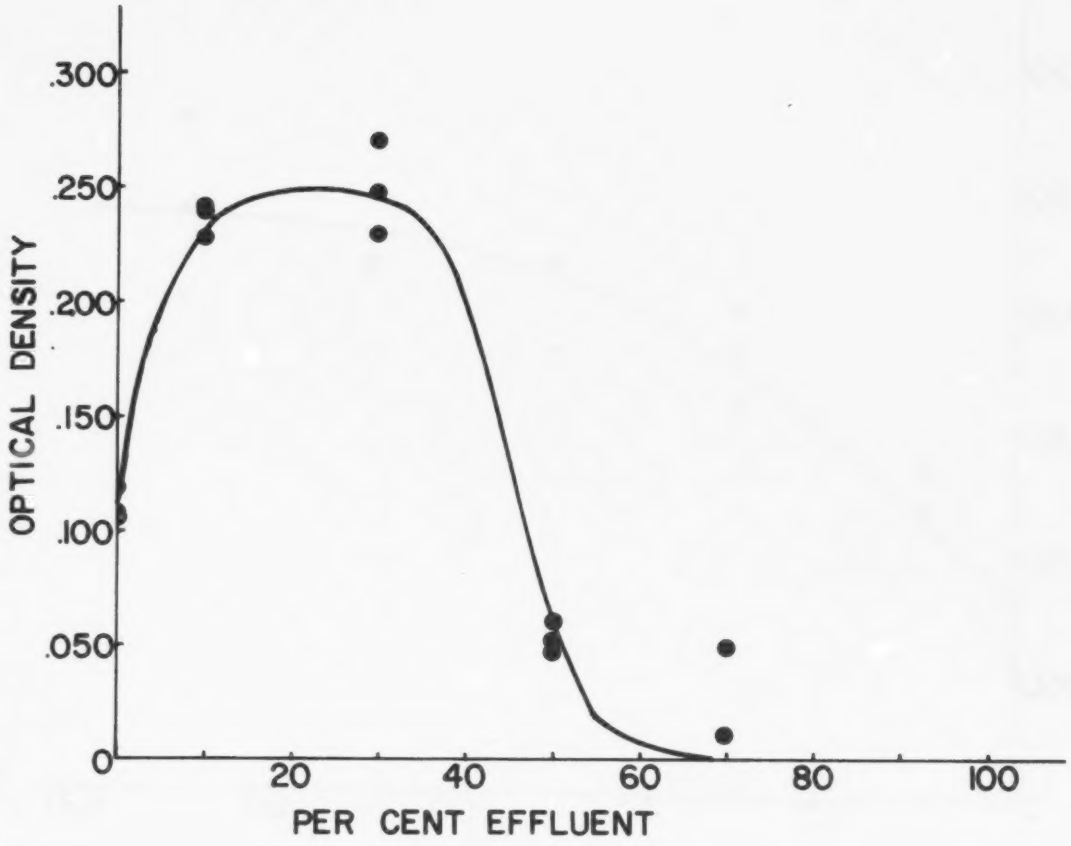


Figure 15. Effects of Textile W effluent on growth of Skeletonema costatum.

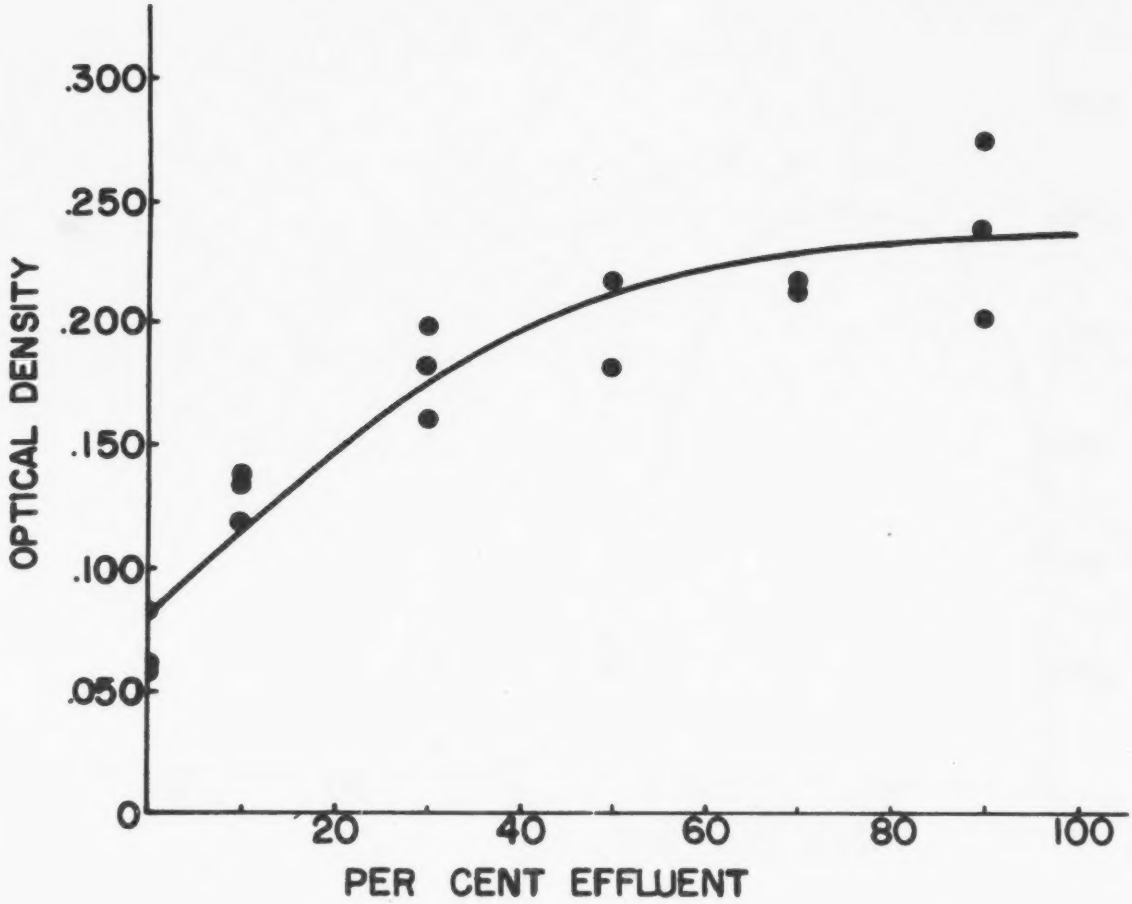


Figure 16. Effects of Textile X effluent on growth of Skeletonemá costatum.

TABLE 3. RELATIVE TOXICITY OF FIVE TEXTILE WASTES TO *P. PUGIO* AND *C. VARIEGATUS*

Degree of toxicity	Waste	
	P. pugio	*C. variegatus*
Most toxic	C	W
	W	N
	A	A
	N	T
Least toxic	T	C

As the table reflects, Waste T was least toxic to *P. pugio*, with the LC50 of 34.5 percent. Waste W was most toxic to *C. variegatus*, but its LC50 was 37.5 percent (Table 2). Therefore, for animals, ranking of wastes is according to toxicity to *P. pugio*.

In contrast to the animal data, all wastes can be ranked according to degree of effect in the algal test, although the ranking by stimulation is different from that by inhibition (see Table 4).

TABLE 4. RELATIVE RESPONSES OF *S. COSTATUM* TO 14 TEXTILE WASTES

Degree of effect	Waste	
	Stimulation	Inhibition
Greatest effect	B,X	L
	K	N
	C,U,W	P
	T	W
	S	G
	G	T
	V	K
	F,L,N,P	C
		F
		V
Least effect		B,S,X,U

As shown in Table 4, there is a rough inverse correlation between stimulation and inhibition, although Waste W ranks high on both lists. In general, wastes that were highly stimulatory were not highly inhibitory, and those that were highly inhibitory were not highly stimulatory. It may be inferred from the data that the response of algae to wastes that caused stimulation at low concentrations and inhibition at high concentrations is related to relative amounts of nutrients and toxicants. If true, high concentrations of either may mask effects of the other in some wastes and the potential impact of those wastes on aquatic systems could not be evaluated by simple bioassays. Also, responses of organisms in our bioassays could be the result of synergistic, additive, and antagonistic interactions between components of the complex wastes.

Results of bioassays were analyzed in relation to chemical composition of each waste reported by EPA (1978) (ref. 3). Neither stimulation nor toxicity could be related to color, BOD, COD, or to concentrations of sulfide, phenol, suspended solids, cyanide, organic carbon, total organics extracted with methylene chloride, metals, ammonia, nitrite, nitrate, Kjeldahl nitrogen, ortho-phosphate, or total phosphorus.

It is not surprising that chemical analyses did not indicate toxicity of wastes. For example, we have found (unpublished data) that the EC50 of nickel and aluminum to several algae is approximately 2 parts per million (ppm) in the absence of a chelator. In the presence of each other, or of an organic material such as the pesticide 2,4-D, toxicities of the metals were reduced. Waste X contained 7 ppm nickel and 640 ppm aluminum in suspended solids and 0.006 ppm nickel and 8.2 ppm aluminum in filtered effluent – enough to inhibit growth completely. It also contained 45 other metals and diethyl phthalate; bis (2-ethylhexyl) phthalate; hexachlorobenzene; 1,1,1-trichloroethane; toluene; ethylbenzene; 1,1,2,2-tetrachloroethylene; and phenol. In spite of this large number of metals and organic compounds, Waste X did not inhibit algal growth or kill animals. It did, however, stimulate algal growth.

Our toxic waste data suggest that effects of a complex effluent are the result of interactions among toxicants and between toxicants and growth stimulators. Potential impact of a complex waste on aquatic systems may or may not be predicted from either chemical or biological tests alone. It must be assumed that, after a waste is dumped into a receiving body, the individual components separate spatially and the total impact may be greater than that indicated by laboratory bioassay.

We suggest that the potential impact of complex industrial wastes be assessed in two ways: (1) bioassays should be used to assess the potential impact of the whole waste on aquatic systems; and (2) after chemical analysis of each waste, bioassays should be performed on components that may be bioactive. If the whole waste or any of its components has an effect, then that waste must be considered for application of treatment technology.

Wastes reported here that stimulated algae at low concentrations (B, C, G, K, S, T, U, V, W, and X), were toxic to algae at low concentrations (L, P, and N) or were toxic to animals would be ranked high on the list of those that require treatment. Wastes C and W were stimulatory to algae and toxic to animals. The combination of algal, shrimp, and fish bioassays indicate that all wastes, with the possible exception of E, require treatment. However, even Waste E caused 40 percent of the shrimp to die and is suspect.

CONCLUSIONS

1. Algae were more sensitive indicators of potential environmental effects of textile wastes than were shrimp or fish.
2. Algal response to each waste was either (a) inhibition of growth, (b) stimulation of growth, or (c) stimulation at low concentrations and inhibition at high concentrations. Fish and shrimp were killed by some wastes.
3. Potential impacts of the wastes on aquatic systems were death of animals, inhibition of algal growth, and stimulation of algal growth, which can lead to establishment of eutrophic conditions.
4. It is suggested that, after complex wastes enter receiving waters, their constituents may be separated spatially, so that effects of individual substances may occur at sites removed from the source.
5. All wastes tested were bioactive toward algae. Since bioactivity of the complex mixtures could not be related to chemical composition, we suggest: (a) bioassays should be used to assess the potential impact of the whole waste on aquatic systems, and (b) after chemical analysis, bioassays should be performed on components that may be bioactive to aid in application of treatment technology.

ACKNOWLEDGMENTS

We thank Sharon Edmisten and Shelley Alexander for their technical assistance. Bioassays on *P. pugio* and *C. variegatus* were done at the EG&G Bionomics Marine Laboratory, Pensacola, Florida, under EPA Contract 68-02-1874.

REFERENCES

1. U.S. Department of Commerce, *Population and Economic Activity in the United States and Standard Metropolitan Statistical Areas, Historical and Projected, 1950-2020*, Bureau of Economic Analysis, Washington, DC., PB-216607, distributed by National Technical Information Service, Springfield, VA, 544 pp., 1972.
2. U.S. Environmental Protection Agency, *IERL-RTP Procedures Manual: Level 1*, "Environmental Assessment Biological Tests for Pilot Studies," Industrial Environmental Research Laboratory, Research Triangle Park, NC, EPA-600/7-77-043, 106 pp., 1977.
3. U.S. Environmental Protection Agency, "Source Assessment: Textile Plant Wastewater Toxics Study," Phase I, Industrial Environmental Research Laboratory, Research Triangle Park, NC, 1978.

FRESHWATER TOXICITY TESTS RELATED TO THE TEXTILE INDUSTRY

William B. Horning, II*, Timothy W. Neiheisel†

Abstract

Freshwater toxicity tests were conducted on samples of secondary treated wastewaters from 23 textile mills as part of a joint U.S. Environmental Protection Agency (EPA) and American Textile Manufacturers Institute (ATMI) study of the textile industry. The primary tests were (1) 96-h static acute toxicity tests with fathead minnows, (2) 48-h static acute toxicity tests with Daphnia pulex *and (3) the algal assay test. These tests were among a series of ecological screening tests for potential aquatic toxicity. The sublethal gill-purge rate (GPR) test with bluegill sunfish was conducted as a supplemental test on four of the textile-mill effluent samples.*

Thirteen of the textile samples indicated acute toxicity. Seven samples were acutely toxic to both fathead minnows and Daphnia pulex. *One was acutely toxic to fathead minnows only, and five were acutely toxic only to* Daphnia pulex. *Ninety-six-hour* LC_{50} *values ranged from 19.0 to 64.7 percent effluent for fathead minnows. Forty-eight-hour* EC_{50} *values ranged from 0 percent survival in all dilutions to 81.7 percent effluent for* Daphnia pulex. *In all cases, most of the toxicity was exerted within the first 24 hours. Extending the length of test periods beyond 24 hours did not appreciably alter* LC_{50} *or* EC_{50} *values.*

The textile effluents were given two separate relative rankings for each of the two species tested. One was based on toxicity and considered only the fathead minnow LC_{50} *and the* Daphnia pulex *48-h* EC_{50} *values. The other included both toxicity and the waste discharge volume, which were used to calculate a daily toxicity discharge expressed as million lethal units/day (MLU/d). The order in the two ranking schemes was different. Several samples, indicating relatively high acute toxicity (low* LC_{50} *values), are shown on a million lethal units/day basis to be of less potential environmental hazard than some other samples exhibiting relatively low acute toxicity.*

In the algal assay test, textile effluent samples that were acutely toxic to fathead minnows, Daphnia pulex, *or both, either stimulated or inhibited algal cultures in 20 percent dilution or less. Six were inhibitory and seven were stimulatory. Of the four samples evaluated with the GPR test, only one elicited a response.*

INTRODUCTION

In 1971, the U.S. Environmental Protection Agency published a state-of-the-art document for waste treatment in the textile industry (ref. 1). Also a development document, the *Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Textile Mills* was published by the U.S. Environmental Protection Agency in 1974 (ref. 2). Neither document addresses the issue of textile waste toxicity. Both discuss various waste treatment systems and their applicability to the textile industry. The development document speaks in terms of effluent quality that can be attained by applying best practical control technology currently available (BPCTCA). The guidelines were based on this premise, and treatment to meet them was to be achieved by July 1, 1977. Treatment to achieve best available technology economically achievable (BATEA) by July 1, 1983, was recommended. However, all of the technologies considered are concerned primarily with reducing the BOD_5, COD, total suspended solids, oil and grease, color, chromium, sulfide, phenols, fecal coliforms, pH, acidity, and alkalinity being discharged into navigable waters. No attempt was made to develop guidelines to include limitations based on the toxicity of textile wastes.

---

*Chief, Newtown Fish Toxicology Station, U.S. EPA, Cincinatti, OH.

†Research Aquatic Biologist, Newtown Fish Toxicology Station, U.S. EPA, Cincinatti, OH.

The U.S. Environmental Protection Agency's Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina, (IERL-RTP) became involved in a joint study with the American Textile Manufacturers Institute (ATMI) (EPA Grant No. 804329) to determine BATEA for textile plant wastewaters. This study focused on only a limited number of pollutants, i.e., BOD_5, COD, color, sulfides, total suspended solids, phenol, and pH. Twenty-three textile mills having well-operated secondary wastewater treatment facilities and representing eight textile-processing categories were selected for the study.

A consent decree (resulting from National Resources Defense Council et al. versus Train) was issued by the U.S. District Court of Washington, D.C., on June 7, 1976. The decree required EPA to enhance development of effluent standards and focused Federal water pollution control efforts on potentially toxic and hazardous pollutants. As a response EPA developed a list of 129 specific compounds (priority pollutants) to be considered during the standards-setting process. EPA decided to conduct a parallel study to the ATMI/EPA grant study, in which the objective was to determine both the removal efficiencies for the 129 consent decree priority pollutants and the reduction in toxicity by six tertiary treatment technologies being investigated under the original grant study.

Phase I of the overall textile wastewater study was designed to establish baseline data for toxicity and the level of priority pollutants present in raw wastewater and secondary effluents at the 23 textile plants (ref. 3). These data were used to screen the 23 plants and to select those plants with toxic effluents for further study. It is important to note that the toxicity tests were designed only to evaluate the reduction in wastewater toxicity by control technologies, and not to evaluate potential environmental impact of these wastes on receiving waters.

This paper presents a discussion of results from static acute toxicity tests with fathead minnows and *Daphnia pulex* and the algal assay bottle tests. These tests were among a battery of ecological and health effects screening tests that were used to evaluate toxicity of the textile wastewaters. The sublethal gill purge rate (GPR) test with bluegill sunfish was also performed on several samples at the Newtown Fish Toxicology Station as a supplementary test and part of our own research program on complex effluents.

In order to evaluate the potential environmental hazard of textile plant wastewater discharges, the acute toxicity data were combined with the effluent discharge volume to provide a daily toxicity discharge rate labelled million lethal units per day. This rate allows a comparison of the relative importance of both toxicity and volume of discharge.

METHODS

Eight individual grab samples of secondary effluent were collected at equally spaced time intervals during the normal working day at each textile mill. Average hydraulic retention time in the various wastewater treatment plants ranged from 1 to 30 days, with an average of 5 days. Equal portions of each of the eight grab samples were combined to make one composite sample for chemical and biological analyses. Chemical analyses included the criteria pollutants and the 129 priority pollutants. Aliquots of the composite samples were iced and shipped air freight to the Newtown Fish Toxicology Station, Cincinnati, Ohio, and to the EPA Environmental Research Laboratory, Corvallis, Oregon.

Ninety-six- and forty-eight-h static acute toxicity tests were conducted with fathead minnows and *Daphnia pulex*, respectively, at the Newtown Fish Toxicology Station. These tests were performed according to the protocols described by Duke (ref. 4). The Algal Assay Bottle Test, using *Selenastrum capricornutum* Printz as the test organism, was performed at the Environmental Research Laboratory, Corvallis, Oregon according to procedures essentially described by Duke.

Seven effluent concentrations, ranging from 100 to 7.8 percent, and a control were used in the static acute toxicity tests. Probit or moving-average-angle statistical procedures were used to calculate estimated LC_{50} and EC_{50} values from the static acute toxicity tests. For comparative purposes in this presentation, the acute 96-h LC_{50} and 48-h EC_{50} values were quantified to a daily toxicity discharge expressed as million lethal units per day. Quantification can be achieved by defining lethal units per gallon (LU/g) as follows:

$$\text{LU/g} = \frac{100\%}{\text{LC}_{50} \text{ or } \text{EC}_{50} \text{ (in percent)}}$$

then,

$$\text{LU/g} \times \text{effluent flow (mgd)} = \text{MLU/d}.$$

Thus, the toxicity data are quantified into units comparable to pounds of BOD_5. The analogy between BOD_5 and toxicity control is essentially identical because in each case an organism's response is used to measure the combined effects from unknown materials in unknown quantities.

The algal growth response was measured as net biomass produced. The response was expressed as percent stimulation or inhibition at the 20 percent wastewater concentration, as compared to growth in a control sample.

The gill purge rate test was done with only four of the textile-mill effluents used in the static acute toxicity tests. The gill purge rate is determined by placing individual fish in a chamber having a stainless steel electrode at each end. The bioelectric potential associated with breathing (ventilation) movement is electronically recorded, and strip chart recordings are visually counted for gill purges. The gill purges show up as a higher than usual spike in the normal breathing record or as a spike with a double peak.

The equipment and procedures used in the present study were similar to those described by Carlson and Drummond (ref. 5) with the following exceptions. The test concentrations were 75, 25, 8.3, 2.7, and 0.9 percent effluent plus a control. Four fish were exposed in 4 liters of solution at each concentration and control water. Gill purge rates of each fish were determined for five 10-min periods over a 12- to 24-h preexposure period. Gill purge rates were determined in the same manner between 12 and 24 hours after initial exposure and again between 36 and 48 hours. Dunnett's 1-sided t-test was used to determine a significant change in gill purge rate at the 0.05 probability level (ref. 6).

RESULTS AND DISCUSSION

The acute effects of the 23 textile plants

TABLE 1. TEXTILE PLANT WASTEWATERS: STATIC ACUTE TESTS INDICATING TOXICITY AND THE ALGAL ASSAY BOTTLE TEST

	Fathead minnow		Daphnia pulex		Algal assay bottle test	
Effluent sample	96-hr LC_{50} % effluent	MLU/d	48-h EC_{50} % effluent	MLU/d	Inhibition/ stimulation	% effluent
A	19.0	1.1	9.0	2.2	I	20
C	46.5	2.2	41.0	2.4	S	20
E	NAT	–	7.8	25.6	I	20
F*	NAT	–	81.7	2.4	S	20
G	64.7	3.2	62.4	3.2	S	20
L*	23.5	3.2	28.0	2.7	I	10
M	NAT	–	60.0	15.3	S	20
N	48.8	2.1	<7.8†	–	I	20
T*	46.5	1.3	NAT	–	S	20
U	NAT	–	12.1	2.5	S	20
V	36.0	2.2	9.4	8.5	S	20
W	55.2	0.5	6.3	4.0	I	10
Z	NAT	–	42.6	4.6	I	20

* gill purge test samples.

† 100 percent dead in all test dilutions.

Note: NAT = no acute toxicity; I = inhibition; S = stimulation.

wastewaters are summarized and discussed in the EPA publication, *Source Assessment: Textile Plant Wastewater Toxics Study, Phase I* (ref. 3). Briefly, the data indicate that 8 textile effluents were acutely toxic to the fathead minnow and 12 were acutely toxic to *Daphnia pulex* (Table 1). Effluent from one plant (T) was acutely toxic to the fathead minnow and not to *Daphnia pulex*. Effluent from five textile plants was acutely toxic to *Daphnia pulex* and not to the fathead minnow. In five of the seven cases where the wastes were toxic to both species, the sensitivity of the two tests was essentially the same.

Direct comparison of the algal assay bottle-test data with the animal-test data is not possible because the highest dilution tested with algae was only 20 percent. However, as shown in Table 1, the 13 samples that were acutely toxic to the fathead minnow, *Daphnia pulex*, or both, either inhibited or stimulated algal growth at 20 percent dilution or less. Six of these wastes were inhibitory, and seven were stimulatory. Additionally, algal growth was stimulated by the nine samples that did not acutely affect fathead minnows or *Daphnia pulex*. Thus, a battery of tests, using different organisms, better represents the effects of a waste on aquatic organisms than a single species test.

Closer examination of the data suggests several significant aspects frequently overlooked when interpreting results from acute toxicity tests. In all cases where the textile effluents were acutely toxic, most of the toxicity was exerted within the first 24 hours (Table 2). Extending the length of the test periods beyond 24 hours did not significantly affect the LC_{50} or EC_{50} values. Eleven previous onsite studies, representing eight different industrial categories, have shown similar results with well-designed and -operated industrial wastewater treatment systems (Table 3). Thus, there are good indications that 24-h acute toxicity tests are sufficient for initial screening purposes.

The textile effluent samples can be ranked on a relative basis from most toxic to least toxic based on fathead minnow LC_{50} and/or *Daphnia pulex* EC_{50} values (Table 4). However, this ranking system does not necessarily indicate the relative potential hazard of the individual effluents to the aquatic environment. When the effluents are ranked, based on mil-

TABLE 2. TEXTILE PLANT WASTEWATERS: ACUTE TOXICITY TIME COMPARISON

	Fathead minnow			Daphnia pulex	
Effluent sample	24-h LC_{50} % effluent	48-h LC_{50} % effluent	96-h LC_{50} % effluent	24-h EC_{50} % effluent	48-h EC_{50} % effluent
A	24.6	19.0	19.0	15.0	9.0
C	46.5	46.5	46.5	41.0	41.0
E	NAT	NAT	NAT	12.6	7.8
F	NAT	NAT	NAT	91.8	81.7
G	68.2	68.2	64.7	64.4	62.4
L	37.5	32.5	23.5	36.0	28.0
M	NAT	NAT	NAT	60	60
N	55.2	48.5	48.8	< 7.8*	<7.8*
T	63.1	46.5	46.5	NAT	NAT
U	NAT	NAT	NAT	20.5	12.1
V	39.1	37.5	36.0	11.5	9.4
W	68.2	66.4	55.2	could not calculate	6.3
Z	NAT	NAT	NAT	63.4	42.6

*100 percent dead in all test dilutions.

Note: NAT = no acute toxicity.

TABLE 3. INDUSTRIAL PLANT WASTEWATER: INCREASES IN TOXICITY TO FISH BETWEEN 24 AND 96 HOURS IN STATIC ACUTE TESTS OF TREATED EFFLUENT FROM 11 INDUSTRIAL PLANTS

Effluent source	Number of samples tested	Number of samples showing toxicity 24-h	96-h	Number of samples showing increased toxicity	Number of samples statistically showing a significant increase
Rubber-rainwear plant	4	4	4	4	0
Oil refinery	10	1	3	3	2
Metal-plating company A	18	3	3	2	1
Metal-plating company B	9	6	6	0	0
Paper company A	2	2	2	0	0
Paper company B	2	0	2	2	0
Glass works	2	0	0	0	0
Aluminum company B	4	0	0	0	0
Carpet mill	6	2	4	3	0
Organic chemical plant A	3	3	3	3	2
Organic chemical plant B	5	0	2	2	0

lion lethal units/day (total amount of toxicity discharged), the relative order is significantly altered (Table 4). For example, effluent A is shown to be one of the most acutely toxic (LC_{50} = 19.0 percent) to fathead minnows, based on LC_{50} values, but is less of a potential threat to the environment on a million lethal units/day basis. The opposite situation occurs with effluent G (LC_{50} = 64.7 percent). (The differences between the two ranking systems are more striking with *Daphnia pulex.)*

The lethal-unit concept considers the units of toxicity as being analagous to BOD_{50}. This provides a means for evaluating the capabilities of a wastewater treatment system to remove total acute toxicity as is done in determining BOD_{50} reductions. All that is required is determining toxicity before and after treatment, quantifying the data into lethal units, and making a comparison. Additionally, million lethal units/day appears to be a realistic means of expressing the potential environmental impact for a specific discharge on the receiving stream. To assess the acutal impact of a waste in a given situation, receiving-stream flow must be considered.

The gill purge is considered to be part of the normal gill cleaning reflex of fish, in which water is forcefully and rapidly flushed across the gills in the same direction as in normal breathing or in the reverse direction. The gill purge rate has been shown to increase when fish are exposed to suspended solids, some pure chemicals, and complex effluents. The response can be observed visually as well as by recording changes in bioelectric potential associated with breathing.

Three of the four textile effluent samples (F, T, K) did not elicit any significant increase in the bluegill gill purge rate. In addition, sample

TABLE 4. TEXTILE PLANT EFFLUENTS: RELATIVE RANKINGS BASED ON 96-HOUR FATHEAD MINNOW LC_{50} VALUES, 48-HOUR DAPHNIA PULEX EC_{50} VALUES, AND MILLION LETHAL UNITS PER DAY

	Fathead minnow		Daphnia pulex	
	LC_{50}	MLU/d	EC_{50}	MLU/d
Most			W	
toxic	A	G,L		E
	L	C,V	E	M
	V	N	A	V
	C,T	T	V	Z
	N	A	U	W
	W	W	L	G
	G		C	L
			Z	U
			M	C,F
			G	A
Least			F	
toxic				

K was not acutely toxic to either fathead minnows or *Daphnia pulex*. In all cases, the fish survived, including those exposed to 75 percent effluent. However, effluent sample L did cause a significant response in 75 and 25 percent dilutions. This sample, as indicated previously, was acutely toxic to both fathead minnows (96-h LC_{50} = 23.5 percent) and *Daphnia pulex* (49-h EC_{50} = 28.0 percent). Sample F indicated low acute toxicity (48-h EC_{50} = 81.7 percent) to *Daphnia pulex*, and sample T was moderately toxic to fathead minnows (96-h LC_{50} = 46.5 percent). As indicated previously, the bluegills showed no response to these effluents. The gill purge rate tests are generally believed to be more sensitive and to indicate toxicity at lower concentrations than acute lethal toxicity tests. This suggests that the bluegills were less sensitive to the toxic materials present in samples F, L, and T than were the fathead minnows and *Daphnia pulex*.

Thus, the usefulness of a battery of tests for biologically evaluating the toxicity of complex wastes is further demonstrated. It is apparent that not all organisms or all tests are equally sensitive to all chemicals or wastes.

REFERENCES

1. U.S. Environmental Protection Agency, *State-of-the-Art of Textile Waste Treatment*, U.S. Environmental Protection Agency Report 12090 ECS 02/71, February 1971.
2. U.S. Environmental Protection Agency, *Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Textile Mills, Point Source Category*, U.S. Environmental Protection Agency Report 440/1-74-022-a, June 1974.
3. G. D. Rawlings, *Source Assessment: Textile Plant Wastewater Toxics Study, Phase I*, U.S. Environmental Protection Agency Report 600/2-78-004h, March 1978.
4. K. M. Duke, M. E. Davis, and A. J. Dennis, *IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests for Pilot Studies*, U.S. Environmental Protection Agency Report 600/7-77-043, April 1977.
5. R. W. Carlson, and R. A. Drummond, "Fish Cough Response—A Method for Evaluat-

ing Quality of Treated Complex Effluents," *Water Res.*, No. 12, pp. 1-6, 1978.

6. Allen L. Edwards, *Experimental Design in Psychological Research*, Holt, Reinhart and Winston, Inc., New York, 488 pp., 1972.

EFFLUENT GUIDELINES DIVISION PROCEDURES FOR MEASURING PRIORITY POLLUTANTS

Roger D. Holm*

Abstract

Priority pollutant compounds are arranged into several groups, each requiring a different mode of approach. Volatile compounds that can be sparged from water at room temperature are concentrated from 5 ml of water onto a collection tube and then transferred onto a chromatographic column of analysis. Less volatile compounds are extracted from wastewater using methylene chloride in the case of basic, neutral, and acid compounds, and hexane-methylene chloride for pesticides. Extracts are concentrated to 1 ml to achieve 1,000- or 2,000-fold concentration enhancement. Except for the pesticides, all organic analyses are carried out using gas chromatography/mass spectrometry (GCMS) techniques. A brief introduction to the technique will be given. Examples of real samples will be provided. Pesticides are characterized using gas chromatography (GC) with electron capture detection. Metals are measured using atomic absorption and inductively coupled argon plasma (ICAP) spectrometry.

In this paper I would like to tell you about the steps we, at Monsanto, take in analyzing priority pollutants. I shall introduce examples of the classes of compounds currently being measured, and then provide a brief introduction to the type of data supplied by the GCMS instrumentation, our most powerful tool in resolving and identifying compounds. Following this discussion, the analytical steps for the volatile compounds that can be sparged from water, the base-neutral and acid compounds obtainable by methylene chloride extraction, the pesticides obtainable by largely hexane extraction, and the metals shall be considered.

Let me begin by illustrating (Figure 1) typical compounds or classes encountered in priority pollutant analyses. Each category requires a somewhat different analysis approach. The volatile compounds are those that can be quantitatively sparged from water and recovered under certain conditions. Examples are carbon tetrachloride and chloroform. The next group contains less volatile materials that are extractable into methylene chloride. At a pH above 11, the base-neutral fraction will contain neutral compounds such as chlorobenzene and phthalate esters, which seem to be everywhere, and amines such as dichlorobenzidine or nitrosoamines. Phenols are extractable from acid solution. Pesticides such as DDT are extracted in a separate scheme. Lastly, metals such as Pb, Hg, and Cd are also included among the priority pollutants.

To aid us later on in understanding the illustrations, I want to consider the type of data obtained from a gas chromatographic mass spectrometer.

A small sample is injected by syringe into the chromatograph. Various solute compounds exit from the instrument at different times. The mass spectrometer measures and can display the fragmentation pattern behavior of these compounds as they issue from the chromatograph. Figure 2 shows five mass spectra obtained at 8-s intervals for a sample. Mass number is displayed along the abscissa. Note that a new compound having two strong masses has appeared in the third scan, and reached a maximum in the fourth scan.

Figure 3 shows a similar series of successive mass spectra in a 3-dimensional display. Time and accumulated scan number proceed along the x-axis; the mass number from 60 to 180 atomic mass units is shown along the y-axis; and signal amplitude is shown on the z-axis. The display is that of dioctyl phthalate, which produces two strong masses at 149 and 167 as it elutes. In this example, I want to develop the concept of a changing panorama of mass frag-

---

*Group Leader, Monsanto Research Corporation, Dayton, OH.

Preceding page blank

- VOLATILE COMPOUNDS
  - CARBON TETRACHLORIDE
  - HALOMETHANES, -ETHANES, -PROPANES
- BASE-NEUTRAL COMPOUNDS
  - CHLOROBENZENES
  - POLYNUCLEAR AROMATICS
  - PHTHALATES
  - NITROSOAMINES
- ACID COMPOUNDS
  - CHLORO- AND NITROPHENOLS
- PESTICIDES
  - CHLORINATED COMPOUNDS
  - POLYCHLORINATED BIPHENYLS
- METALS
  - HEAVY METALS
  - CYANIDE

Figure 1. Representative classes and compounds among the priority pollutants.

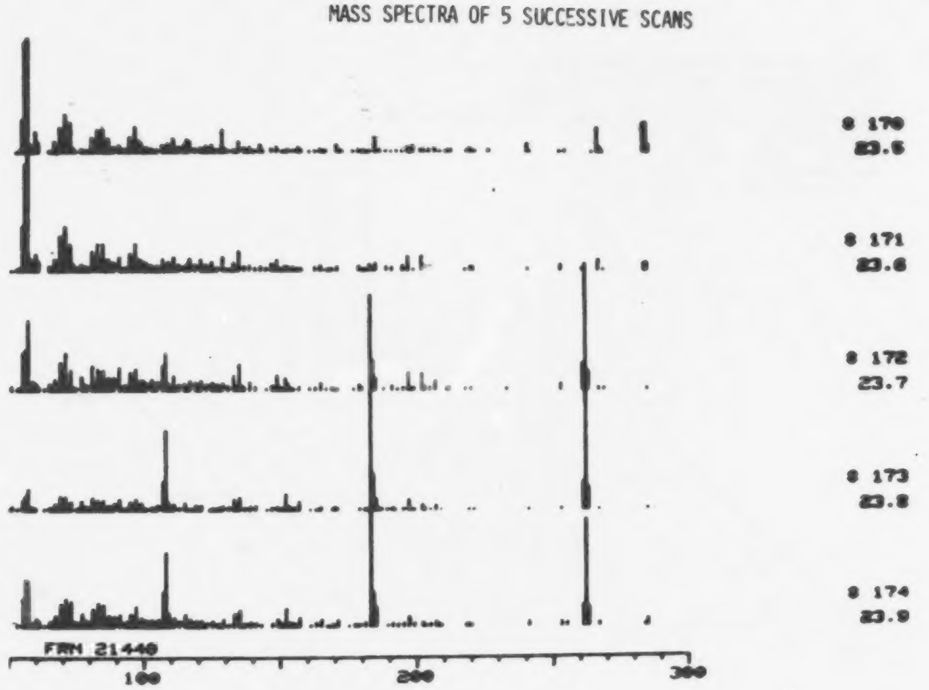


Figure 2. Successive mass spectra scans as compounds elute from the gas chromatograph.

ments as chemicals elute from the chromatograph. The computer software can connect the peaks of the respective masses of each scan to form a reconstructed chromatogram for an individual mass, which is shown in Figure 4.

In this figure the capability is illustrated for the mass range 140 to 180 amu. We have here a chromatogram in which the data system is displaying the appearance of mass 149. It can be seen that here dioctylphthalate eluted around scan number 196, about 27 minutes from the start. In general, the compound identity is determined by characteristic mass fragments, its appearance at the appropriate time in the chromatogram, and relative mass intensities standing in the same ratios as those of standard compounds. We have considered the production of these ion mass chromatograms because we shall use them frequently during the remainder of this talk.

Let us consider now the analysis of the volatile components of the priority pollutants. Small vials of wastewater are collected with care to avoid air bubbles. In the lab the water is spiked with an internal standard, and it is sparged for 12 minutes in a helium stream flowing at 40 ml/minute.

The compounds are swept from the solution onto a collection tube and are adsorbed on Tenax-GC porous polymer. At the end of 12 minutes, the collection tube is heated to transfer the compounds onto the head of a cold chromatographic column. After 4 minutes of heated desorption, the chromatograph run is started and the column temperature is raised slowly to 170° C.

Compounds elute at different times. In Figure 5 three volatile compounds are shown. The chloroform is eluted at about 15 minutes. We can tell it is chloroform by its characteristic retention time and by its two significant masses at 83 and 85 amu. It can be seen that 1,1,2-trichloroethane elutes later, also producing significant fragments with masses of 83

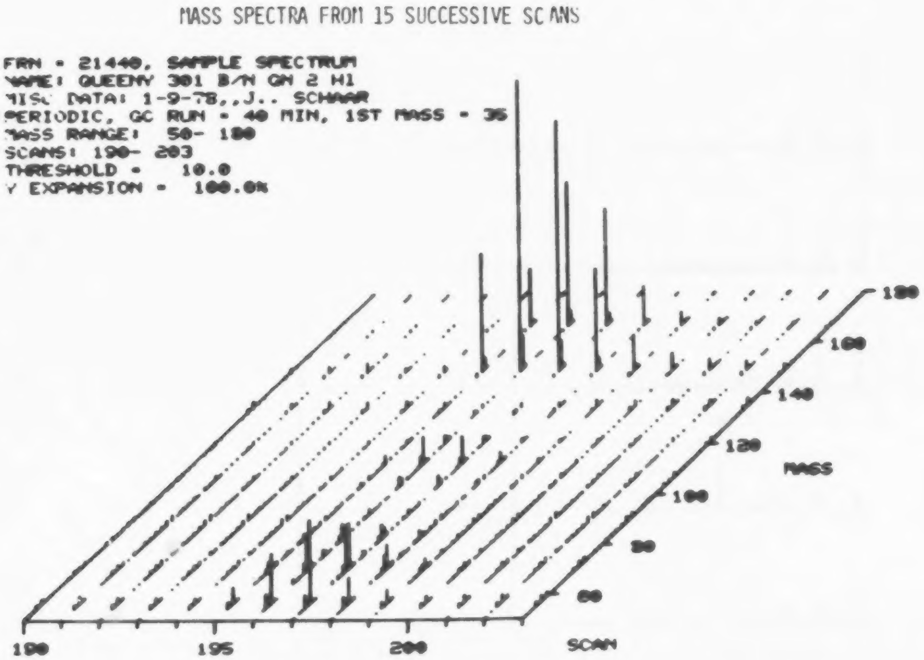


Figure 3. Three-dimensional view of successive mass spectral scans of bis(2-ethylhexyl)-phthalate centered at scan 196.

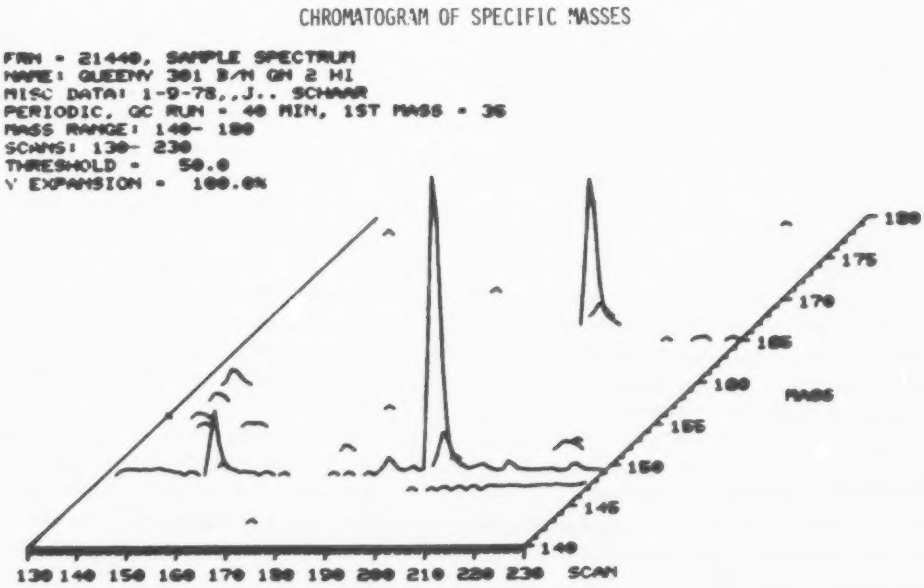


Figure 4. Three-dimensional view of ion mass chromatogram for bis(2-ethylhexyl)-phthalate centered at scan 196.

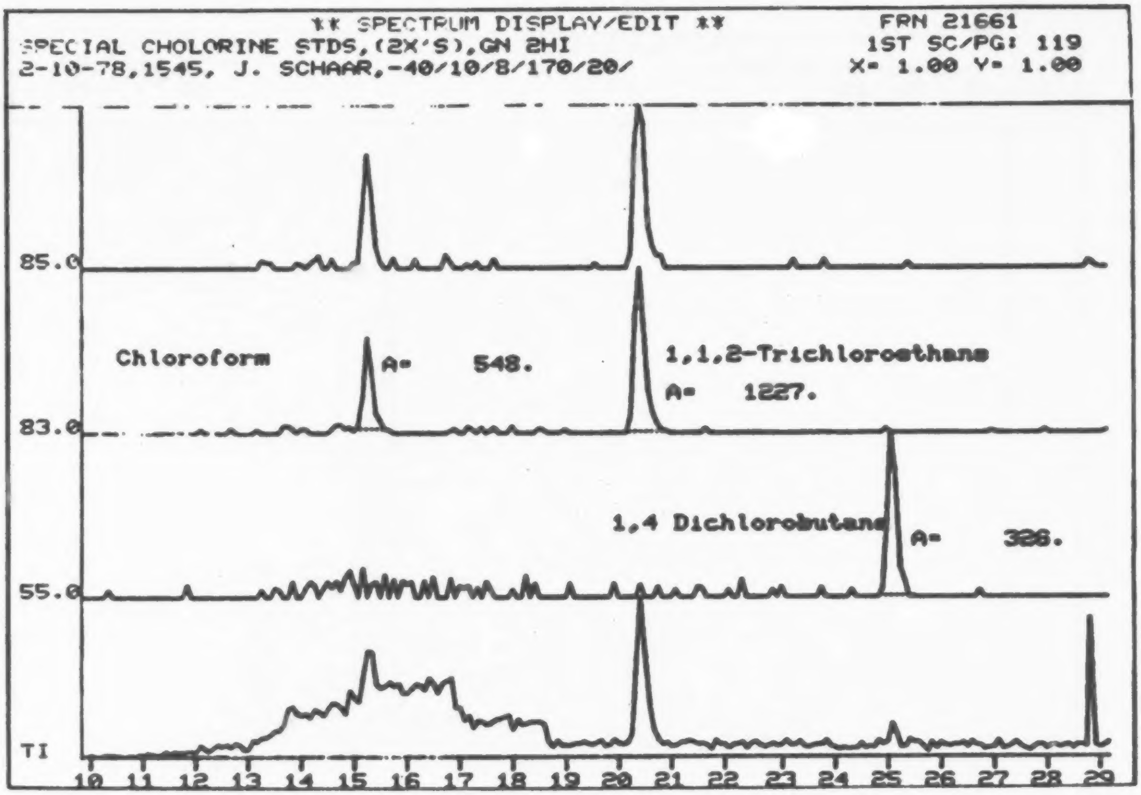


Figure 5. Display of ion mass chromatograms for three volatile compounds.

and 85. The ratio of intensity, however, is different. For confirmation, a third mass, 97 in the case of 1,1,2-trichloroethane, must also be observed, and the spectrum must match that of the standard.

Finally Figure 6 illustrates a real sample having 13 volatile priority pollutants. In this case the total ion current of the detector is plotted vs. time to provide a chromatogram display.

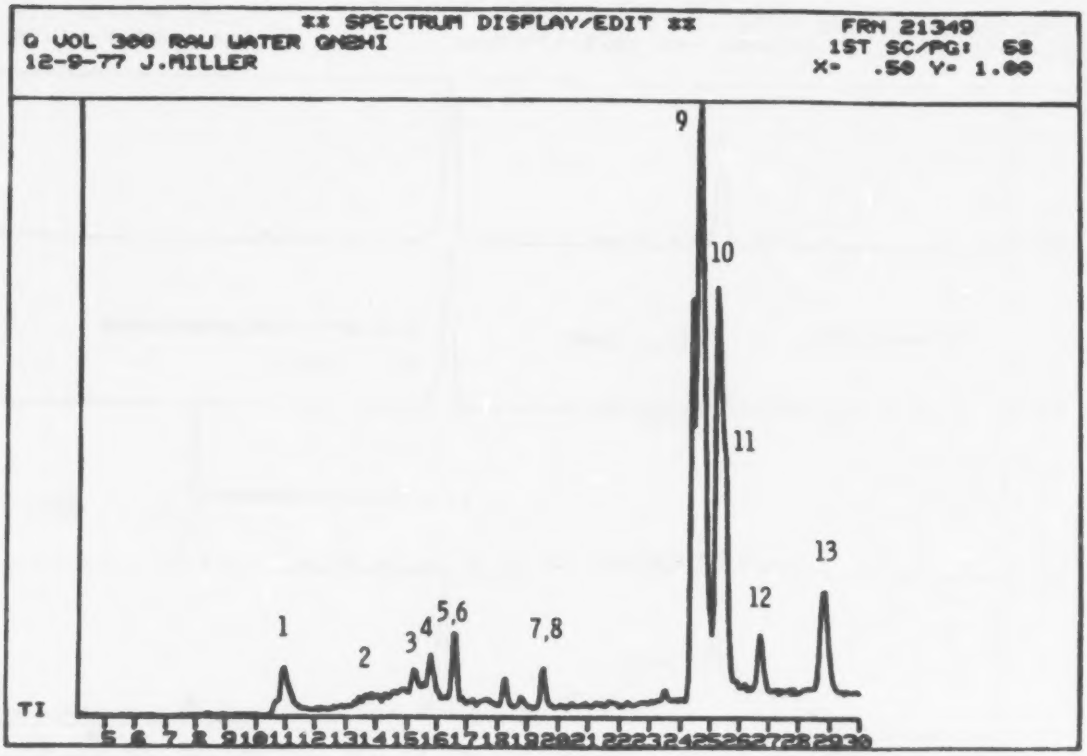
Let us turn to the extractable compounds not volatile enough to be quantitatively sparged. The steps are summarized in Figure 7.

Our procedure is to extract a 2-liter sample, adjusted to pH 11, with methylene chloride. Neutral compounds and basic amines will concentrate in the methylene chloride, and the phenols and acids will remain in the water as salts. The organic layer is removed, dried, and concentrated ultimately to 1 milliliter. The aqueous solution containing the phenols is then acidified to pH 2 and extracted again. The extracts are concentrated, also to 1 milliliter. In this way a 2,000-fold concentration enhancement is achieved.

Figure 8 shows a 2-liter extraction in process. Figure 9 shows the extract in the process of evaporation using a Kuderna-Danish evaporator.

Upon analysis the base-neutral concentrate may appear relatively complex, as is shown in Figure 10. Hidden among many of these peaks are quite a number of polynuclear aromatics. This sample was from an aluminum plant.

Figure 11 illustrates the total ion trace of a wastewater extract which had a great number of compounds merging together as they eluted



1 methylene chloride
2 bromochloromethane
3 chloroform
4 1,2-dichloroethane
5 1,1,1-trichloroethane
6 carbon tetrachloride
7 trichloroethylene
8 benzene
9 1,1,2,2-tetrachloroethene
10 toluene
11 1,4-dichlorobutane
12 chlorobenzene
13 ethylbenzene

Figure 6. Total ion chromatogram of a volatile sample.

from the chromatograph. Despite all the compounds, only two priority pollutants were observed, however, in this sample.

In Figure 12 the lower plot is the total ion chromatogram we saw before. The peak with mass 149 at 27 minutes is bis (2-ethylhexyl) phthalate. The small peak at 19 minutes is d_{10}-anthracene, which was added as an internal standard for quantifications.

A significant effort goes into data interpretation, and an example will illustrate this. Figure 13 shows the mass spectrum of the material eluting at this time. The hydrocarbon background shown in this figure can be removed in the interactive computer-based data interpretation process to give the resulting mass spectrum of the material alone. Thus, Figure 14 shows the three characteristic masses of d_{10}-anthracene at 188, 94, and 106.

Figure 15 shows phenols observed in an acid sample. The extraction from acid solution and workup are identical to those of the base-neutral fraction. In this case five phenols were observed, some hidden beneath the envelope.

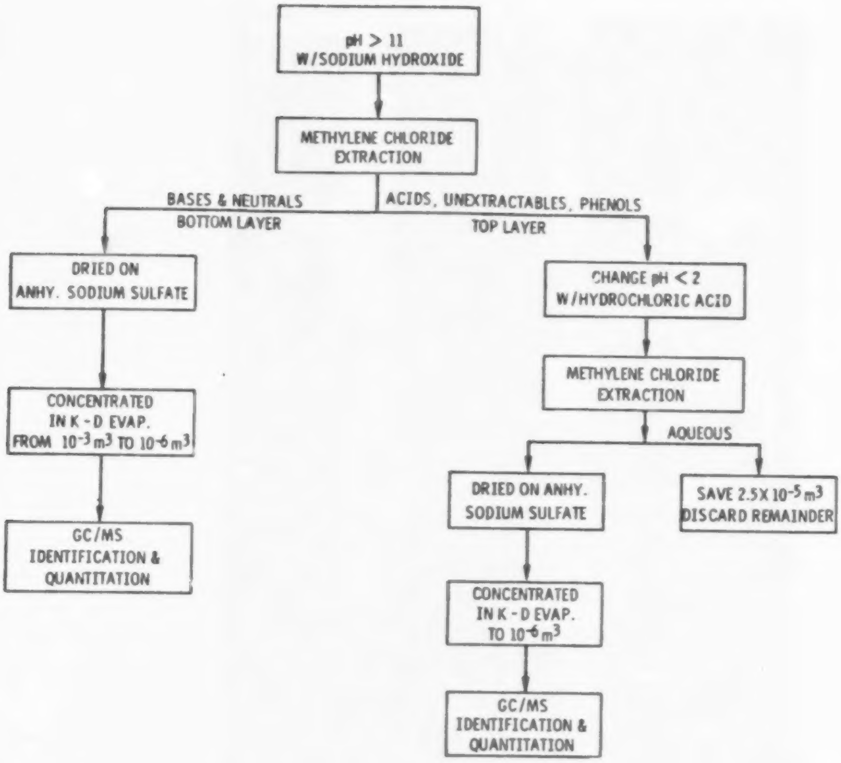

pH > 11
W/SODIUM HYDROXIDE
METHYLENE CHLORIDE EXTRACTION
BASES & NEUTRALS
BOTTOM LAYER
ACIDS, UNEXTRACTABLES, PHENOLS
TOP LAYER
DRIED ON ANHY. SODIUM SULFATE
CONCENTRATED IN K - D EVAP. FROM 10-3 m3 TO 10-6 m3
GC/MS IDENTIFICATION & QUANTITATION
CHANGE pH < 2 W/HYDROCHLORIC ACID
METHYLENE CHLORIDE EXTRACTION
AQUEOUS
DRIED ON ANHY. SODIUM SULFATE
SAVE 2.5 X 10-5 m3 DISCARD REMAINDER
CONCENTRATED IN K - D EVAP. TO 10-6 m3
GC/MS IDENTIFICATION & QUANTITATION

Figure 7. Extraction and workup scheme for base-neutral and acid compounds.

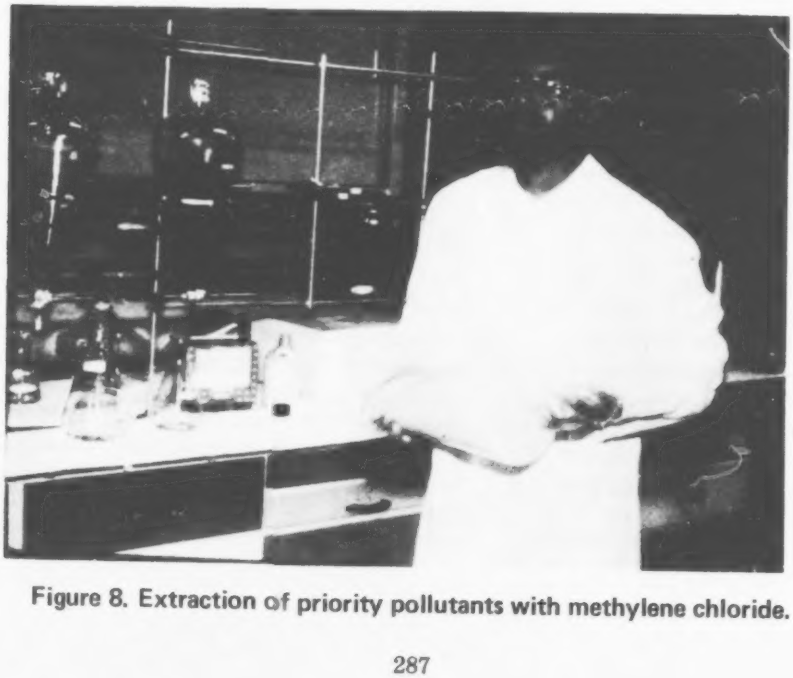


Figure 8. Extraction of priority pollutants with methylene chloride.

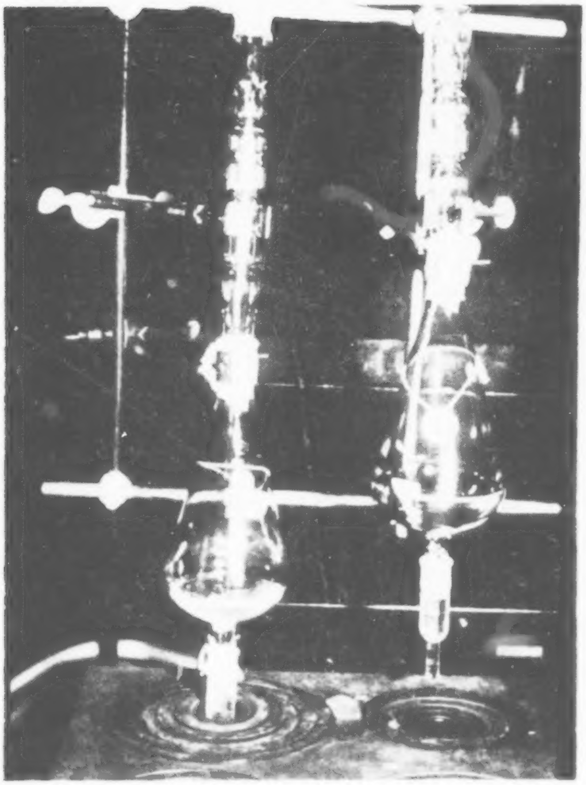


Figure 9. Kuderna-Danish evaporator to reduce methylene chloride extract volume.

These were phenol, 2-nitrophenol, 2,6-dimethylphenol, 4-nitrophenol, and pentachlorophenol.

A variety of steps are taken to maintain quality control in these analyses. Organic free water is periodically run through the entire extraction and cleanup process to ensure that nothing is picked up in the laboratory operations. Duplicate runs are periodically made, including samples divided in the field and sent to the lab as blind duplicates. An internal standard is always added during the evaporation stage. R-values, relative response values used in quantification, are checked with standards periodically to maintain accuracy and to ensure proper instrumentation performance. Our experience with extractable compounds has been that for a measurement performed in triplicate, the reported value should lie within 34 percent of the true value 90 percent of the time. Bear in mind that extraction efficiencies in many waste solutions are not known, but evidence suggests recoveries ranging from 10 percent to 100 percent, with many in the 30 percent to 80 percent range.

Pesticides are extracted using the method in the *Federal Register.* Generally cleanup is required to remove from solution nonpesticides that cause significant detector response. Figure 16 shows a typical pesticide chromatogram using the electron capture detector before the second-stage cleanup. The peaks indicated were removed by an acetonitrile back ex-

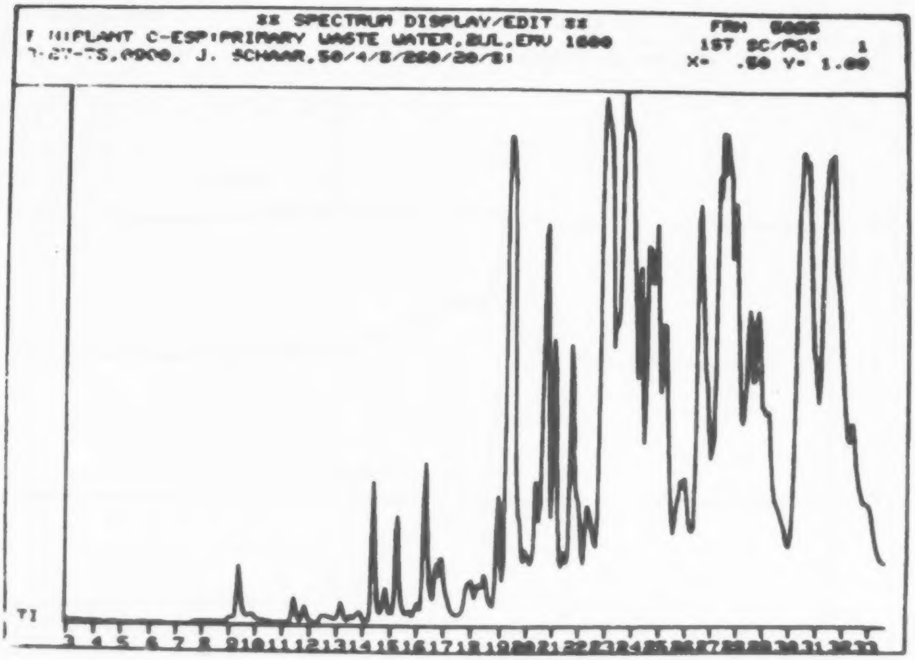


Figure 10. Typical total ion chromatogram of a base-neutral fraction.

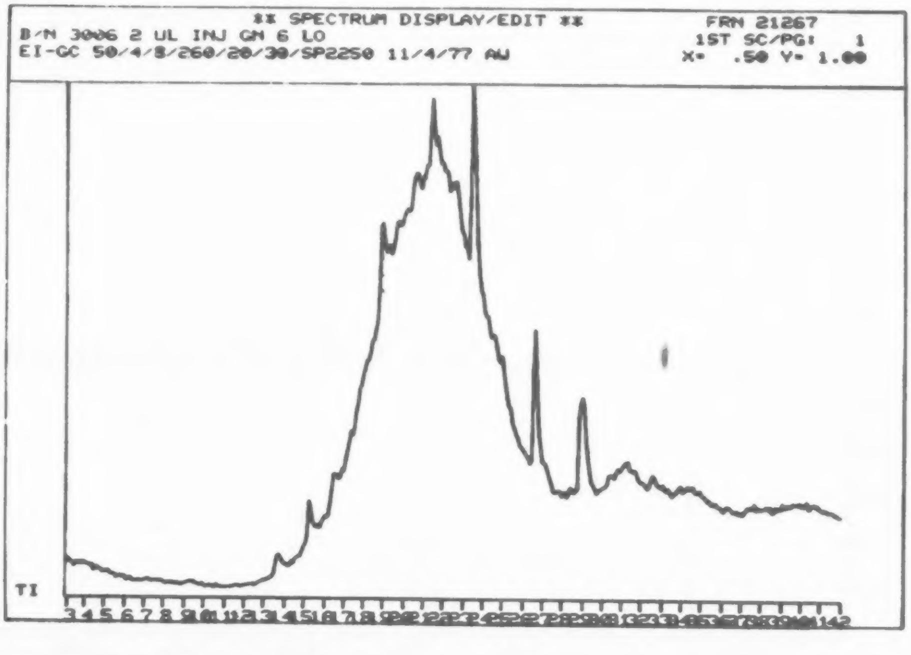
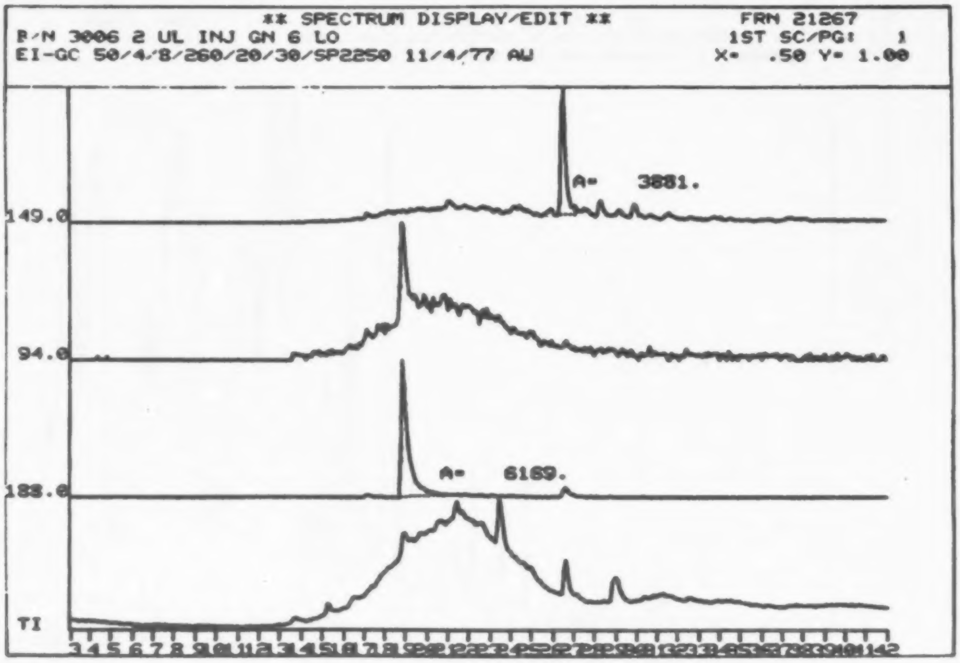


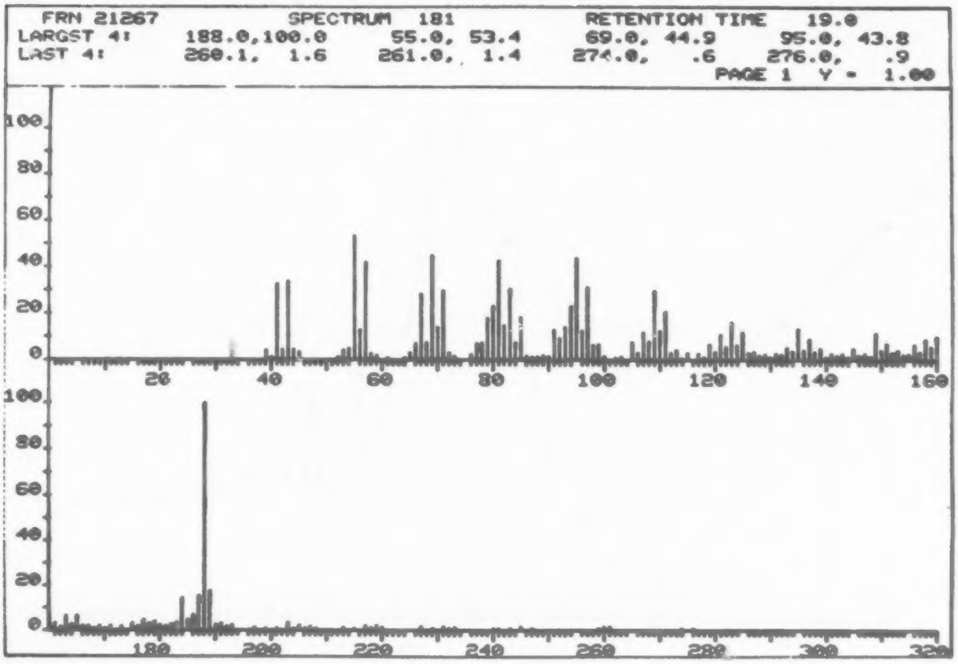
Figure 11. Total ion plot of a base-neutral sample illustrating overlapping peaks.



```
                 ** SPECTRUM DISPLAY/EDIT **              FRN 21267
B/N 3006 2 UL INJ GN 6 LO                                1ST SC/PG:    1
EI-GC 50/4/8/260/20/30/SP2250 11/4/77 AW                 X=   .50 Y= 1.00
```

Monsanto

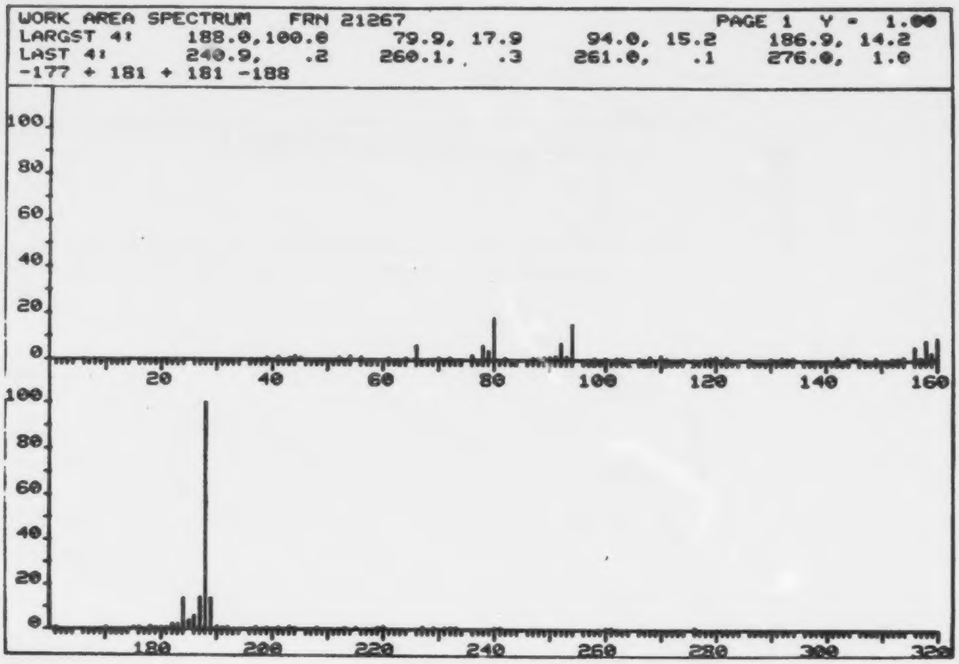
Figure 12. Illustration of individual compounds observed within the same sample.



```
  FRN 21267              SPECTRUM  181            RETENTION TIME   19.0
LARGST 4:      188.0,100.0      55.0, 53.4      69.0, 44.9       95.0, 43.8
LAST 4:        260.1,   1.6    261.0,  1.4     274.0,    .6     276.0,    .9
                                                            PAGE 1  Y =  1.00
```

Monsanto

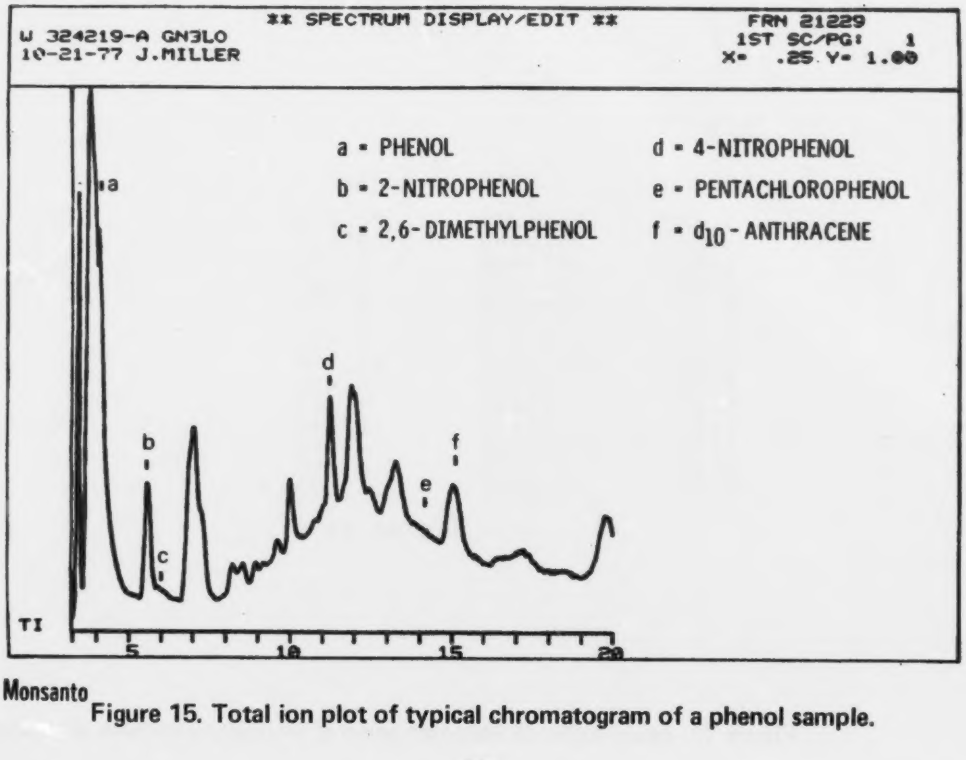
Figure 13. Raw mass spectrum showing d_{10}-anthracene plus hydrocarbon background.



```
WORK AREA SPECTRUM    FRN 21267                                PAGE 1   Y =   1.00
LARGST 4:       188.0,100.0      79.9, 17.9      94.0, 15.2      186.9, 14.2
LAST 4:         240.9,    .2     260.1,   .3     261.0,    .1     276.0,   1.0
-177 + 181 + 181 -188
```

Monsanto

Figure 14. Net mass spectrum of d_{10}-anthracene after removal of background.

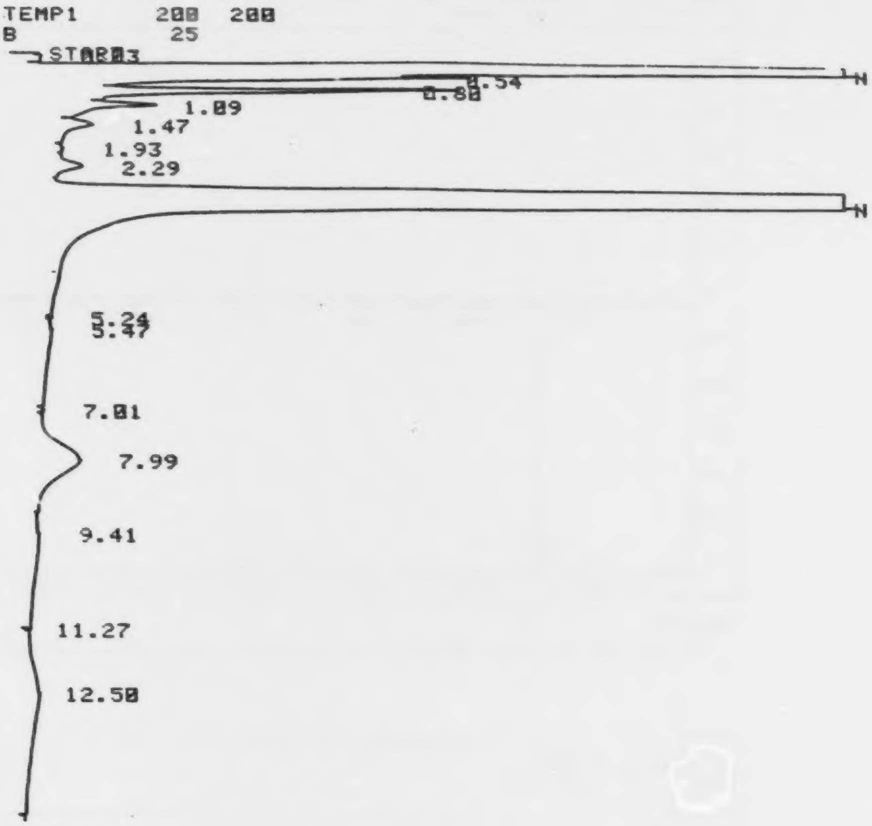


```
                        ** SPECTRUM DISPLAY/EDIT **                FRN 21229
W 324219-A GN3LO                                                   1ST SC/PG:    1
10-21-77 J.MILLER                                                  X=   .25 Y= 1.00
```

Monsanto

Figure 15. Total ion plot of typical chromatogram of a phenol sample.

Monsanto



```
hp 5830A
AREA %

   RT              AREA          AREA %

  0.39         28530000          27.786
  0.54          3242000           3.157
  0.80          3854000           3.753
  1.09          1852000           1.804
  1.47          1386000           1.350
  1.93           347600           0.339
  2.29          1167000           1.137
  3.01         54970000          53.535
  5.24            59320           0.058
  5.47          1705000           1.661
  7.01            51310           0.050
  7.99          3361000           3.273
  9.41           874400           0.852
 12.50          1280000           1.247

              XF:   1.0000 E+ 0
```

Figure 17. Same pesticide chromatogram after back extraction with acetonitrile.

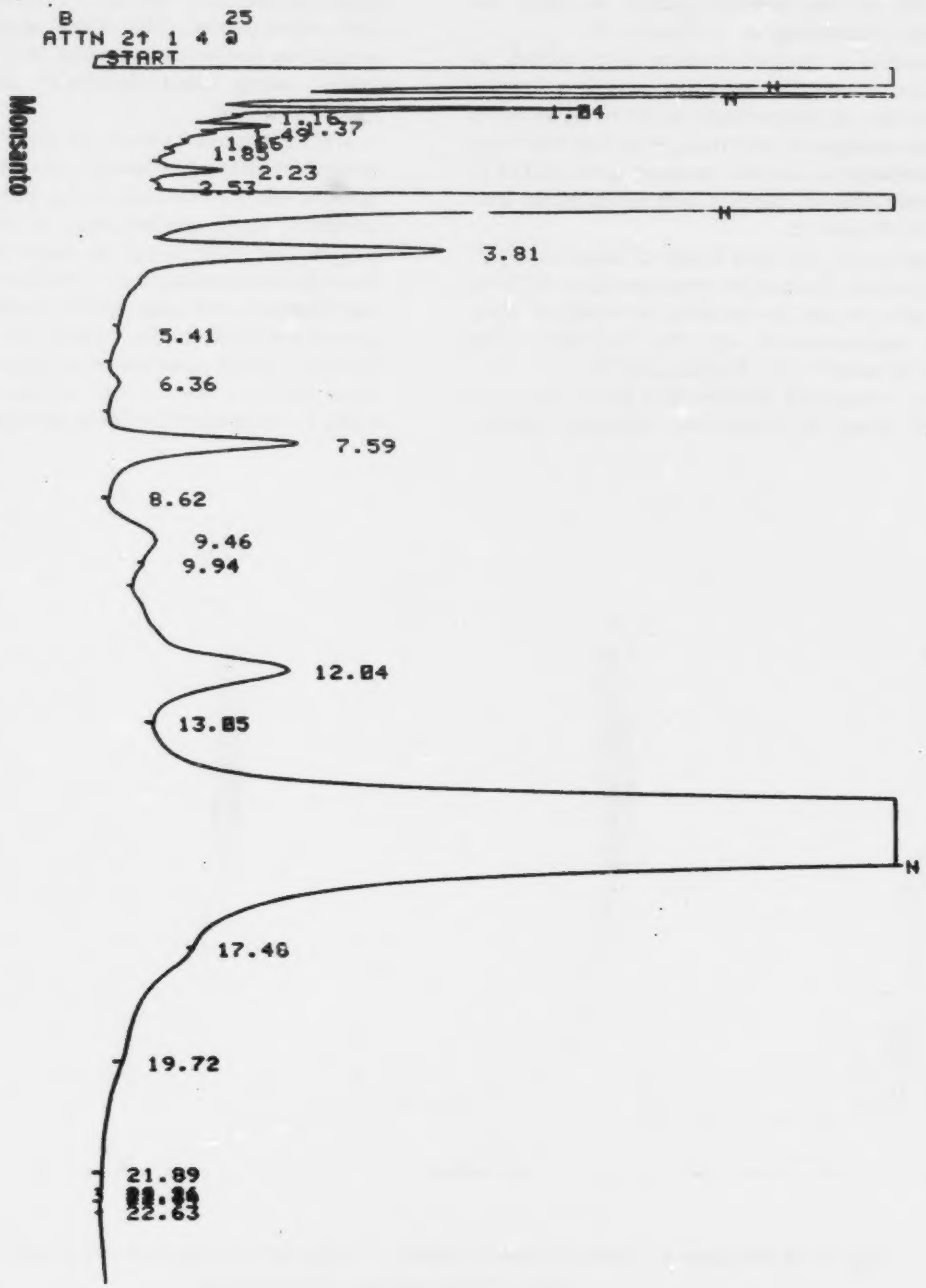


Figure 16. Typical pesticide chromatogram before cleanup.

traction of the hexane extract to yield the cleaner chromatogram in Figure 17.

Sometimes further cleanup is required, involving adsorption on silica gel, plus further separation of components in different solvents having a range of polarities. Note the peak that appeared in the middle chromatogram of the 15 percent ether-85 percent petroleum ether fraction in Figure 18.

Figure 19 lists two types of metal analysis approaches. Metals are measured by acidifying the solution and performing an atomic absorption measurement on the indicated four volatile metals: Hg, Se, As, and Tl.

The remaining metals of concern are measured using an automated emission spectrograph having as a source an inductively coupled argon plasma. This allows simple solution aspiration excitation. Quality control is maintained using blind duplicate samples and spiked samples.

We have looked briefly at several phases of priority pollutant analyses, discussed typical compounds, and looked at the way mass spectrometry data can be used to identify compounds and how it can be selective. Also we have discussed analyses of volatile compounds, the base-neutral and acidic compounds, the pesticides, and metals. There has been little time to expand upon these techniques, but perhaps you now have a feel for the efforts that must be expended for these analyses.

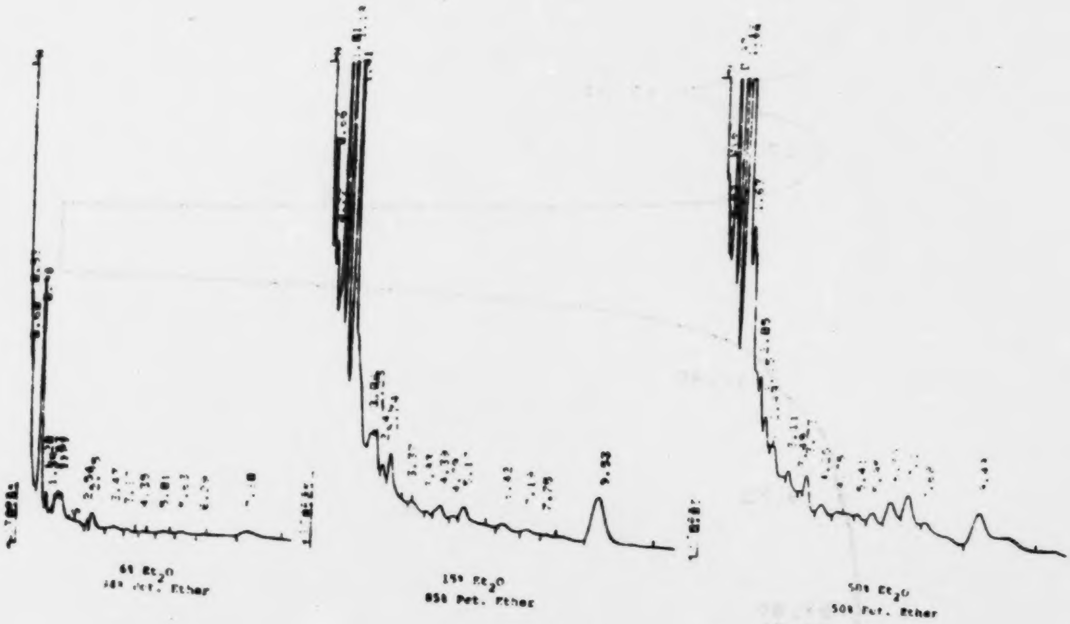


Figure 18. Portions of typical chromatograms of solutions having increasing polarities after Florisil column fractionation.

METALS ANALYSES

- ATOMIC ABSORPTION - (As, Hg, Se, Tl)
- INDUCTIVELY COUPLED ARGON PLASMA (ICAP)

QUALITY CONTROL

- DUPLICATE SAMPLES
- SPIKED SAMPLES

Figure 19. Methods utilized for analysis of priority pollutant metals.

ORGANIC SAMPLING AND ANALYSIS FOR ENVIRONMENTAL ASSESSMENT

Philip L. Levins, Judith C. Harris*

Abstract

Sampling and analysis procedures for organic species have been developed in support of the phased approach to environmental assessment developed by the Process Measurements Branch of EPA, IERL-RTP. These methodology studies focus on process and emission streams.

Level 1 analysis procedures have been evaluated and refined with the objective of providing a methodology suitable for use in any experienced laboratory for the generation of reliable data on most species likely to be encountered. A Level 1 reporting format has been developed which translates the chemical data into terms more readily used in assessing relative hazardousness.

Level 2 sampling and analysis procedures are being developed, based upon both a more comprehensive broad spectrum protocol and upon specific procedures for particular analytes—PAH's and phenols, for example.

INTRODUCTION

Organic sampling and analysis for environmental assessment calls for a phased approach including Level 1 (survey), Level 2 (confirmation), and Level 3 (monitoring) studies. The Level 1 procedures developed by the Process Measurements Branch have been in use for about 2 years and procedures for Level 2 are beginning to be both developed and applied. The purpose of this paper is to discuss two aspects of organic sampling and analysis methodology which are particularly relevant to environmental assessment of textile industry effluents. First, the status of Level 1 organic analysis procedures will be reviewed, with emphasis on the methods of interpreting and reporting the results. The second portion of the paper will deal with the development of alternative methods that are appropriate for Level 2 sampling of polar, water-soluble organics in aqueous effluent streams.

LEVEL 1 ORGANIC ANALYSIS PROCEDURES

The philosophy of the phased approach to environmental assessment and the details of the Level 1 sampling and analysis procedures are described in other EPA publications (refs. 1,2). The objectives and methodology of Level 1 organic analysis are therefore not discussed in detail in this paper.

Level 1 sampling and analysis is designed to provide identification of the major categories of organic compounds and estimation of their concentration in the gaseous, liquid, or solid effluent stream. Organic analyses are done either directly on neat samples, such as gases or organic liquid streams, or on methylene chloride extracts of samples such as aqueous streams, solids, or SASS train sample components. Figure 1 illustrates the overall Level 1 analysis scheme for the organic components. The procedure covers the quantitative analysis of the major volatility classes by the procedures indicated below.

Volatility	Definition	Procedure
Gases	Boiling point < 100° C	Field GC
Volatile	Boiling point 100-300° C	TCO
Nonvolatile	Boiling point > 300° C	GRAV

The TCO procedure is a laboratory gas chromatographic (GC) method for the volatile components. The GRAV procedure is a gravimetric method for the nonvolatile components.

Qualitative analysis to determine the major chemical categories in each sample is performed by first separating the sample according to polarity on a silica gel liquid chromatography (LC) column. Each of the fractions is then identified by obtaining infrared (IR) and low resolution mass spectral (LRMS) data.

---

*Arthur D. Little, Inc., Cambridge, MA.

Preceding page blank

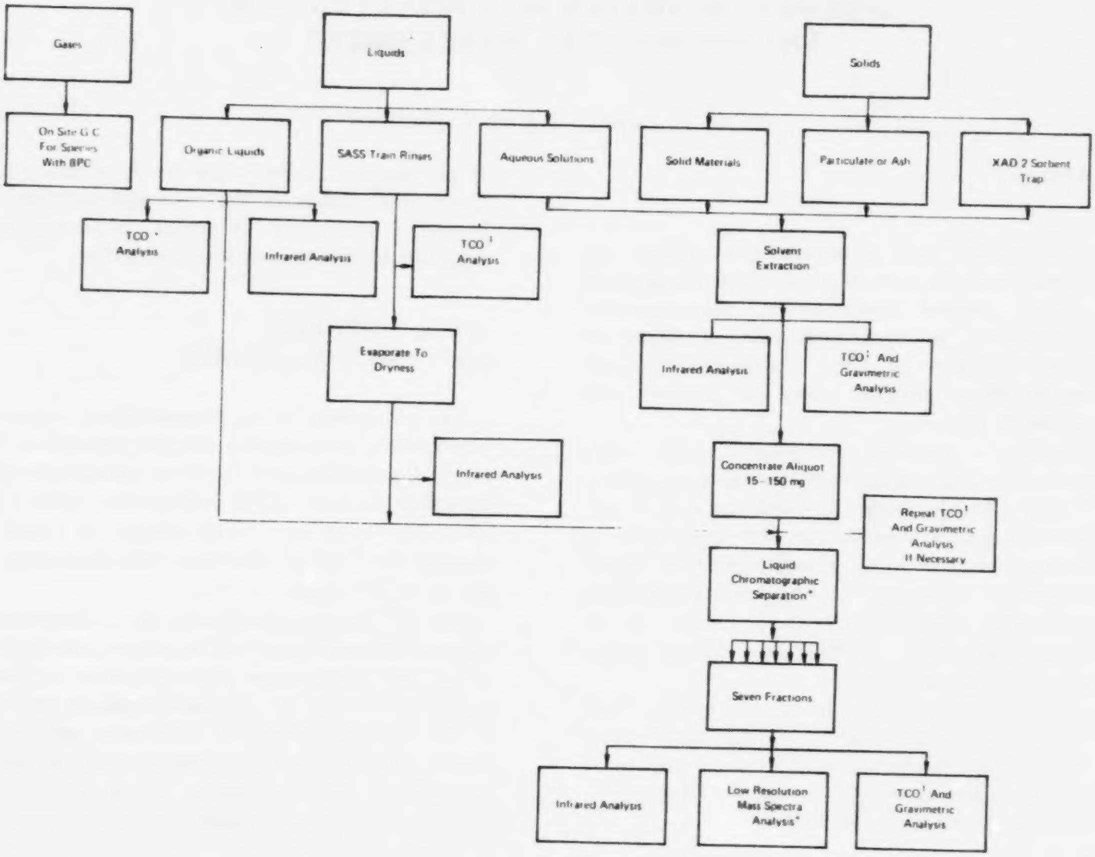

Gases
Liquids
Solids
On Site G C For Species With BPC
Organic Liquids
SASS Train Rinses
Aqueous Solutions
Solid Materials
Particulate or Ash
XAD 2 Sorbent Trap
TCO¹ Analysis
Infrared Analysis
TCO¹ Analysis
Solvent Extraction
Evaporate To Dryness
Infrared Analysis
TCO¹ And Gravimetric Analysis
Infrared Analysis
Concentrate Aliquot 15–150 mg
Repeat TCO¹ And Gravimetric Analysis If Necessary
Liquid Chromatographic Separation*
Seven Fractions
Infrared Analysis
Low Resolution Mass Spectra Analysis*
TCO¹ And Gravimetric Analysis

Figure 1. Level I organic analysis flow diagram.

REPORTING LEVEL 1 ANALYSIS RESULTS

At this time, sufficient Level 1 tests have been run (refs. 3,4,5,6) to verify that the specified organic analysis procedures are capable of identifying a broad range of organic compound categories when present in environmental samples. As the data have been accumulated, it has been possible to develop and recommend with some confidence a format for reporting and summarizing the organic analysis results.

The first complete set of data to be developed in the Level 1 organic analysis are the LC results, which are reported in the form shown in Table 1. The volatile (TCO) and nonvolatile (GRAV) components of each LC fraction are reported after computing back to equivalent quantities in the entire sample. The total quantity of each fraction is then derived from the sum of TCO + GRAV and the concentration in the sampled stream is calculated from the sample quantity and volume sampled.

Results of the IR analysis of each sample and LC fraction are tabulated in terms of the frequency of peak maxima, probable assignment, and intensity (weak, medium, or strong). A typical example is given in Table 2.

The LRMS results are reported in terms of the compound categories found in the sample and their estimated relative abundances. A typical report using this format is shown in Table 3. Most of the subsequent initial Level 1 interpretation of data is done using only the major compound category data. Compound

TABLE 1. EXAMPLE LC REPORT

	TCO mg	GRAV mg	Total mg	Concentration* mg/m^3
Total Sample†	106	386	492	82
Taken for LC‡	23	84	107	18
Recovered#	17	74	91	15
Fraction	**TCO§ mg**	**GRAV§ mg**	**Total§ mg**	**Concentration* mg/m^3**
1	1.4	11.5	13	2.1
2	15	4.6	20	3.3
3	55	259.4	314	52
4	0.5	10.1	11	1.8
5	0.9	31.3	32	5.3
6	3.2	16.6	20	3.3
7	0.5	2.8	3	0.5

*Total mg divided by total volume.

†Quantity in entire sample, determined before LC.

‡Portion of whole sample used for LC, actual mg.

#Quantity recovered from LC column, actual mg.

§Total mg computed back to total sample.

TABLE 2. EXAMPLE IR REPORT

Frequency (cm^{-1})	Intensity	Assignment	Comments
3400	M	OH, NH	Broad
3050	W	Unsaturated CH	
2850,2920	M	Saturated CH	
1710	S	Acid, ketones	
1680	M	Monosub amide, ketones	
1600	M	Ring vibrations	
1450	M	CH_2	
1060	S	Si-O, ether	Broad
740	M	Subst. pyridine, C-Cl	

categories for LRMS interpretation are chosen primarily from a list of about 24 general compound groupings.

For each sample or sample extract subjected to the Level 1 organic analysis procedure, there will be an LC report, eight IR reports, and up to seven LRMS reports. This is an unwieldy body of data from which to make a decision. To reduce these data to a workable form, the detailed information from the combined LC, IR, and LRMS data is combined into a summary report. The organic extract summary report basically tabulates the identity and quantity of all compound categories found in each of the LC fractions and sums them, to yield an estimate of source concentrations. The results from the sample shown in Table 4, for instance, indicated a high concentration of aromatics and some polar compounds in the sampled stream.

The considerable overlap in chemical class composition that is generally expected between adjacent fractions in the Level 1 LC

TABLE 3. EXAMPLE LRMS REPORT

Major categories

Intensity	Category	MW range
100	Ketones	180-280
100	Heterocyclic nitrogen compounds	167-253
10	Esters	
10	Carboxylic acids	
10	Phenols	

Sub-categories, specific compounds

Intensity	Category	m/e	Composition
100	Acridine	179	$C_{13}H_9N$
100	Fluorenone	160	$C_{13}H_8O$
10	Phenol	94	C_6H_6O
10	Cresol	108	C_7H_8O
10	Benzoic Acid	122	$C_7H_6O_2$
10	Carbazole	167	$C_{12}H_9N$
10	Methylacridine	193	$C_{14}H_{11}N$
10	Methylfluorenone	194	$C_{14}H_{10}O$
10	Anthraquinoline	229	$C_{17}H_{11}N$
10	Benzanthrone	230	$C_{17}H_{10}O$
10	Dibenzofluorenone	280	$C_{21}H_{12}O$
10	Dibutylphthalate	278	$C_{16}H_{22}O$
10	Methylbenzanthrone	244	$C_{18}H_{12}O$

Other

scheme is illustrated by the data in Table 4. It is worth emphasizing that this LC procedure is not a high-resolution technique and that its function in Level 1 methodology is to facilitate qualitative analysis by IR and LRMS, rather than to isolate various compound categories in discrete fractions. The reporting format developed takes account of this fact by combining the information obtained on various LC fractions to provide an integrated description of the chemical composition of the sampled stream.

In summary, the procedures developed for interpreting and integrating the Level 1 organic analysis data result in a list of organic chemical classes and their estimated concentrations in the stream sampled. This overall estimate of stream chemistry is appropriate for comparison with decision criteria such as the EPA's Multimedia Environmental Goals for Environmental Assessment (ref. 7).

If one or more of the estimated concentrations exceeds the levels of concern, it may then be desirable to reexamine the organic analysis data in detail to determine more specifically the nature of the material responsible for the positive "trigger."

LEVEL 2 SAMPLING OF WATER-SOLUBLE ORGANICS

The results of the Level 1 organic analysis provide a basis for proceeding with and/or directing more detailed Level 2 studies. Level 2 inquiries are expected to be directed primarily at the identification, quantification, and con-

TABLE 4. ORGANIC EXTRACT SUMMARY TABLE

	Sample: sorbent extract							
	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics, mg/m^3	0.61	0.74	8.4	1.0	0.33	1.5	0.50	13
TCO, mg	5.2	19	73	6.7	3.7	5.3	0.1	110
GRAV, mg	13	3.3	180	23	7.3	41	15	280
Category	Int/mg/m^3							
Sulfur	100/0.6							0.6
Aliphatic HC's	10/0.06							0.06
Aromatics-benzenes		10/0.06						0.06
Fused Arom 216		100/0.6	100/4	100/0.5				5
Fused Arom 216		10/0.06	100/4	100/0.5				5
Heterocycl-c S		10/0.06	10/0.4	10/0.05				0.5
Heterclytic N				10/0.05	/0.1*	100/0.7	10/0.02	1
					/0.01*	10/0.07	100/0.2	0.3
Carboxylic acids					/0.1*	100/0.7	10/0.02	1
Phenols					/0.01*	10/0.07	10/0.02	0.1
Esters					/0.01*	10/0.07		0.08

*Estimated assuming same relative intensities as LC6, since IR spectra of LC5 and LC6 very similar.

firmation of specific compounds whose presence could be inferred on the basis of the categorical analysis of Level 1. Level 2 analyses may be conducted either on samples freshly collected for that purpose or on samples retained from the Level 1 sampling effort. The choice between collecting a new sample or analyzing a retained sample or fraction for the Level 2 data will be highly specific to the exact question to be answered and to the nature of the chemical species to be determined.

Most of the sampling procedures chosen for Level 1 were the best available and are still appropriate for Level 2 studies. On the other hand, there are several organic compound categories for which alternative sampling procedures are required to achieve optimal collection and recovery. Examples that are particularly relevant to textile industry environmental assessment are very polar, water-soluble organics in aqueous effluents. This section of the paper will describe work in progress to characterize sampling approaches for these types of compounds.

Solvent extraction of pH-adjusted samples is the most widely used approach to sampling of organic pollutants in aqueous industrial effluents. This approach, which is specified for Level 1 survey analysis, is capable of giving quantitative recoveries of a wide range of nonpolar organic materials. However, quantitative recovery of very polar, water-soluble organic species is not always achievable by solvent extraction. Estimates of the maximum achievable extraction efficiency can be based on the value of the solvent/water partition coefficient for a particular species. For example, three successive extractions of water sample, using 100 ml of solvent per liter of sample for each extraction, can be expected to provide >90 percent extraction efficiency for individual organic species that have solvent/water partition coefficients >12. Extensive listings of partition coefficients are available (refs. 8,9), and these can be used to verify extraction efficiencies for individual organic species of concern. Some illustrative values, presented in Table 5, indicate that carboxylic acids, sulfonic acids, glycols, and phenols are among the categories of compounds not efficiently extracted.

An attractive alternative approach for collection of organics from large quantities of water is the use of an in situ continuous extractive sampler containing a solid sorbent material. One of the earliest devices of this type, once widely used in the field, was the

TABLE 5. ILLUSTRATIVE VALUES OF SOLVENT: WATER PARTITION COEFFICIENTS*

Compound	$P_{CHCl_3:H_2O}$	$P_{heptane:H_2O}$	$P_{ether:H_2O}$
Efficiently extracted			
Propyl ether	580	34	18
Hexyl amine	490	30	16
Butyl mercaptan	1,200	98	34
Benzene	460	24	15
Chlorobenzene	6,200	1,100	150
Indene	78,000	1,500	180
Acridine	20,000	9,300	575
Thiophene	301	13	10
Inefficiently extracted			
Acetic acid	0.03	1.0	0.4
Phenol	2	0.05	31
Benzene sulfonic acid	0.0001	0.000006	0.002
Ethylene glycol	0.002	0.00001	0.005

*Estimated using data bank and methods of reference 8.

EPA's carbon absorption module (CAM) (ref. 10), with generally good collection efficiency but low recoveries for organics. A number of previous workers (refs. 11,12,13,14) have done laboratory studies on the use of macroporous resins and have determined overall recoveries of selected organic compounds from water, under conditions designed to simulate sampling applications. Other investigators (refs. 15,16) have explored the use of polyurethane foam plugs for collection of organics, especially polycyclic aromatic hydrocarbons. Anion exchange resins have been used successfully in several instances for the concentration of polar or ionizable organic compounds (refs. 17,18). The Ambersorb carbonaceous adsorbents have not yet been extensively researched as possible adsorbents for PAH or other compounds from water.

The present work involves a systematic laboratory investigation of the applicability of macroreticular resins for general and compound-specific sampling of organics, based on small-scale, chromatographic experiments. The basic approach used in this work is the generation and analysis of the frontal breakthrough curve produced by challenging a sorbent cartridge with an aqueous solution of organic analyte at constant flow rate. The experimental method has been described in some detail elsewhere (ref. 19). Figure 2 is a schematic representation of a frontal breakthrough curve, indicating the 50 percent and 100 percent breakthrough points. The frontal breakthrough curve generated in each experiment was analyzed to determine the characteristic 50 percent breakthrough parameters and the adsorption isotherm.

The specific retention volume corresponding to 50 percent breakthrough, V_{50}, is the number of sorbent bed volumes (BV) of aqueous solution that have passed through the bed up to the time when the exit concentration of organic species equals one-half of the challenge concentration. The V_{50} value, which is independent of challenge concentration as long as the latter is sufficiently low, allows one to determine whether an organic compound is retained by a given volume of sorbent at a specified flow rate and sampling time. The weight capacity of the sorbent for organic species, in mg/cm^3 of resin, corresponding to 50-percent breakthrough is given by $V_{50} \times$ challenge concentration. The weight capacity is thus a function of challenge concentration, subject to an upper limit corresponding to saturation of the bed. The weight capacity, while useful for comparisons between laboratory experiments, is less

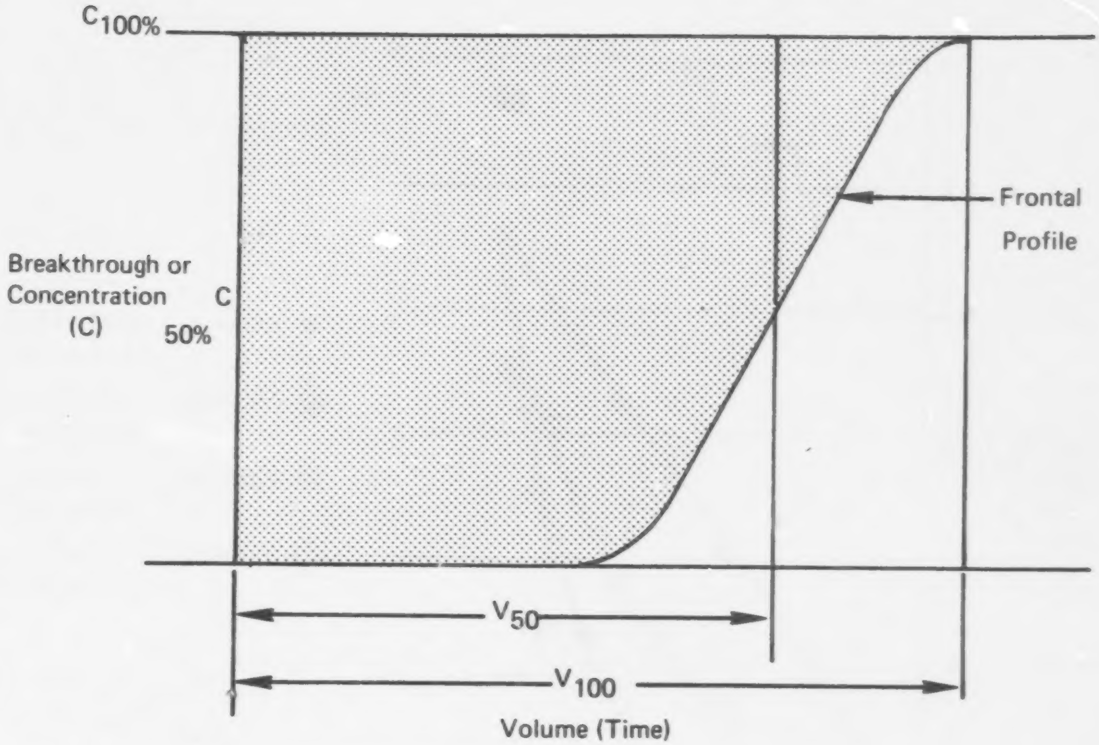


Figure 2. Schematic of frontal breakthrough curve.

valuable than V_{50} as a sampling device design parameter.

The adsorption isotherm, a plot of uptake of solute in mg/cm^3 of resin versus percent breakthrough, was calculated by integrating the area in front of the breakthrough curve at 5, 25, 50, 75, and 100 percent breakthrough. Adsorption isotherms contain valuable information on the affinity of the resin for a sorbate, and allow the saturation capacity of the sorbent to be ascertained. If the breakthrough curve is generated under equilibrium sorption conditions, the isotherm is expected to show a Langmuir shape—linear in the low uptake region and reaching to a plateau corresponding to saturation of the available adsorption sites. Deviation of the isotherm from the expected Langmuir shape is an indication of significant mass transfer effects in the frontal chromatography experiment.

The initial studies in this program were done using XAD-2, the resin most extensively studied for collection of organic species from water. A series of experiments was performed to determine the effect of aqueous sample flow rate on the adsorption of a moderately polar organic species, acetophenone, on XAD-2. As shown in Figure 3, distinctly non-Langmuir isotherms were obtained at sample flow rates corresponding to linear velocities through the sorbent bed of 2 cm/min or higher. Note that the uptake at 50-percent breakthrough is also very much lower at the higher flow rates tested. These flow rate studies clearly show that mass transfer effects have an important impact on adsorption of acetophenone from water onto XAD-2, even at relatively low flow rates. This may indicate that adsorption of species for which XAD-2 has limited affinity, such as acetophenone, is limited by diffusion into the pores of the macroreticular resin particles, while more readily sorbed species, such as polynuclear aromatic hydrocarbons (PAH), are efficiently captured on the exterior surface of

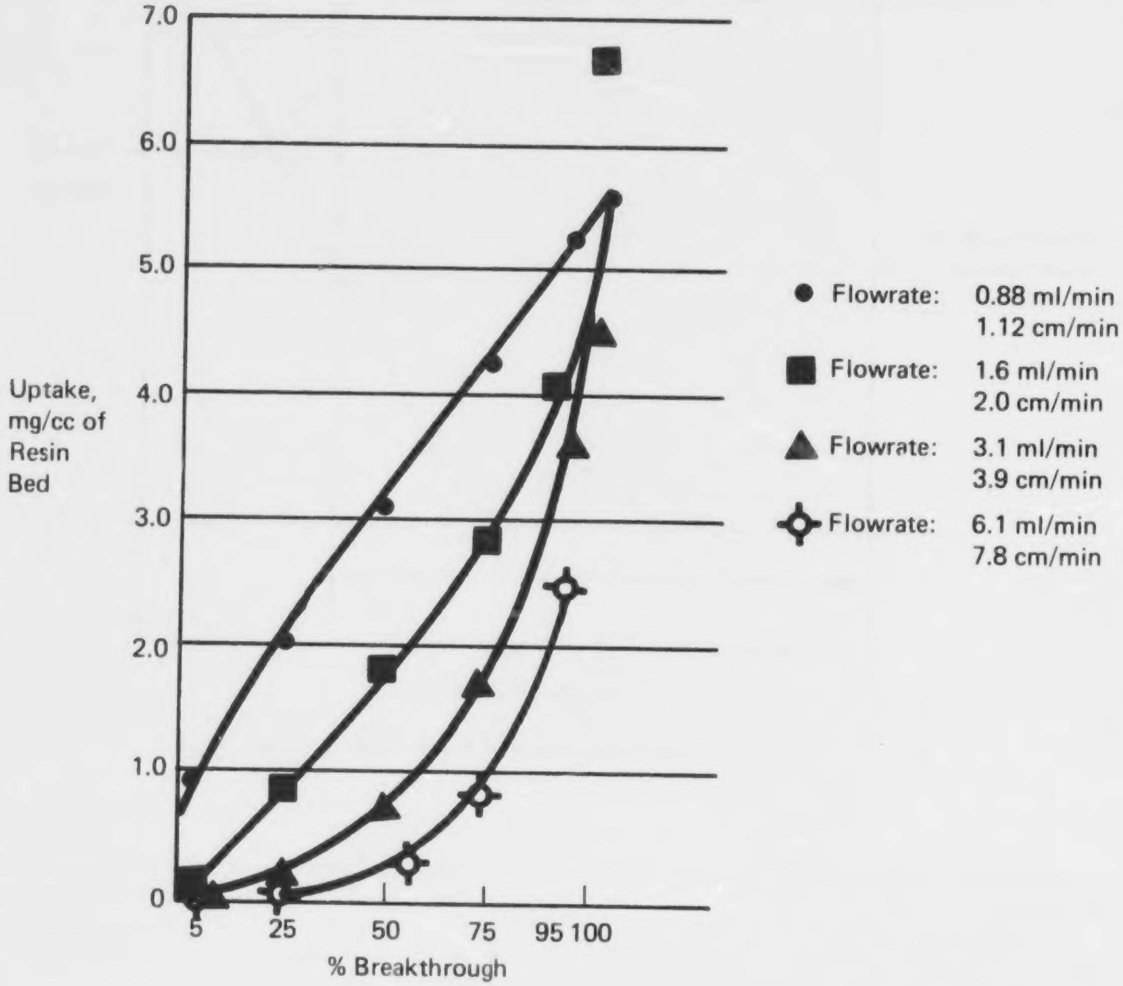


Figure 3. Isotherms for adsorption of acetophenone on XAD-2 from water as a function of flow rate.

the particles. It was necessary to reduce the flow rate to about 1 cm/min linear velocity in order to achieve the expected isotherm shape and maximum uptake. This linear velocity was maintained in subsequent breakthrough experiments with other analytes and sorbents. The flow rate dependence study illustrates the fact that sampling approaches proven effective for PAH in water are often not directly applicable to other organics.

A variety of organic compounds in aqueous solutions were examined to determine their frontal chromatographic behavior on XAD-2. Because of the interest in extrapolating to field sampling of industrial effluents, pH adjustments were not made in these tests. The 50 percent breakthrough parameters are presented in the first column of Table 6. The results confirm the observations of other workers that XAD-2 has a high affinity for nonpolar aromatic species; no measureable breakthrough was obtained for these compounds. The XAD-2 also seems to be an adequate sorbent, for sampling purposes, for species such as

TABLE 6. COMPARISON OF UPTAKE ON VARIOUS RESINS AT 50 PERCENT BREAKTHROUGH FOR 10 PPM CHALLENGE CONCENTRATION

Resin	XAD-2		XAD-7		IRA-904	IRA-93	XE-347
Analyte	Wt. capacity mg/cm3	Vol. capacity BV	Wt. capacity mg/cm3	Vol. capacity BV	Wt. capacity mg/cm3	Wt. capacity mg/cm3	Wt. capacity mg/cm3
Phenol	0.43	74.7	0.60	67.9	(>14.3)[†]	*	*
Benzoic acid	0.54	102	0 [illegible]	39.2	(>14.3)[†]	*	*
Benzyl alcohol	0.53	98.9			0.164		*
Acetophenone	3.2	527	0.89	96.6			(>712)[†]
Chlorobenzene	(>3.8)*						
Methyl benzoate	11.4	1,750					
Naphthalene	(>3.8)*						
Carbazole					0.58[‡]		(>0.72)[†]
Acridine					0.32[‡]		(>1.42)[†]

[*] No breakthrough in 4 hours, therefore, volumetric capacity not determinable. (Number in parenthesis is amount sorbed up to that point.)

[†] No breakthrough in 16 hours, therefore, volumetric capacity not determinable. (Number in parenthesis is amount sorbed up to that point.)

[‡] Uptake at 40 percent breakthrough.

ketones and esters. The low affinity of XAD-2 for very polar organics such as phenol and benzoic acid was confirmed.

Several other macroreticular resins were tested to explore their potential for use as alternatives or supplements to XAD-2 for collection of polar species. The breakthrough parameters for these resins are summarized in Table 6. XAD-7 was found to have higher affinity for phenol, but lower affinity for benzoic acid, than XAD-2.

The ion exchange materials, IRA-904 and IRA-93, showed >10 times more capacity for phenol and benzoic acid in distilled water than did XAD-2 or XAD-7. However, breakthrough on these resins was virtually instantaneous if the aqueous solution contained as much as 250 ppm of sodium chloride, an amount commonly found in aqueous effluents. This is not entirely unexpected in that the manufacturer of these resins recommends use of salt solutions as the most effective regeneration method.

Carbonaceous resin, XE-347, showed a very high affinity for all of the compounds tested. Except for the very polar analytes, no breakthrough was observed over a 16-h period. Investigation of the Ambersorb resins, including quantitative studies of recovery of sorbed material, is continuing. This sorbent medium presently appears to represent a promising approach for sampling of very polar water-soluble organics in aqueous streams.

ACKNOWLEDGEMENTS

This work was performed under EPA Contract No. 68-02-2150 from the Process Measurements Branch, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. The authors wish to thank Ms. Zoe A. Grosser and Ms. Karen C. Weaver for their contributions.

REFERENCES

1. U.S. Environmental Protection Agency, "Environmental Assessment Sampling and Analysis: Phased Approach and Techniques for Level 1," EPA-600/2-77-115, June 1977.
2. U.S. Environmental Protection Agency, *IERL-RTP Procedures Manual: Level 1 Environmental Assessment,* EPA-600/2-76-160a, PB 257-850/AS, June 1976.
3. U.S. Environmental Protection Agency, "Compilation of Level 1 Environmental

Assessment Data," EPA-600/2-78-211, October 1978.

4. N. H. Gaskins and F. W. Sexton, "Additional Chemical Data: A Supplement to Compilation of Level 1 Environmental Assessment Data," report prepared on EPA Contract No. 68-02-2156.
5. U.S. Environmental Protection Agency, "Source Assessment: Textile Plant Wastewater Toxics Study: Phase 1," EPA-600/2-78-004h, March 1978.
6. J. L. Rudolph, J. C. Harris, Z. A. Grosser, and P. L. Levins, "Ferroalloy Process Emissions Measurement," draft report prepared on EPA Contract No. 68-02-2150, August 1978.
7. J. G. Cleland and G. L. Kingsbury, *Multimedia Environmental Goals for Environmental Assessment*, Vol. I, EPA-600/7-77-136a, November 1977.
8. A. Leo, C. Hansch, and D. Elkins, "Partition Coefficients and Their Uses," *Chemical Reviews*, Vol. 71, No. 525, 1971.
9. A. Seidell, *Solubility of Organic Compounds*, Vol. II, 3rd ed., Van Nostrand, Princeton, NJ, 1941.
10. M. J. Taras, A. E. Greenberg, R. D. Hoak, and M. C. Rand, eds., "Organic Contaminants," *Standard Methods for the Examination of Water and Wastewater*, 13th ed., pp. 259-270, American Public Health Association, Washington, DC, 1971.
11. G. A. Junk, J. J. Richard, J. S. Fritz, and H. J. Svec, "Resin Sorption Methods for Monitoring Selected Contaminants in Water," *Identification and Analysis of Organic Pollutants in Water*, L. H. Keith, ed., Ann Arbor Science, Ann Arbor, MI, 1976.
12. P. E. Strup, J. E. Wilkinson, and P. W. Jones, "Trace Analysis of Polycyclic Aromatic Hydrocarbons in Aqueous Systems Using XAD-2 Resin and Capillary Column Gas Chromatography Mass Spectrometry Analysis," *Polynuclear Aromatic Hydrocarbons: Second International Symposium on Analysis, Chemistry and Biology*, P. W. Jones and R. E. Freudenthal, eds., Raven Press, New York, pp. 131-138, 1978.
13. R. G. Webb, "Isolating Organic Water Pollutants: XAD Resins, Urethane Foams, Solvent Extraction," EPA-660/4-75-003, 1975.
14. P. Van Rossum and R. Webb, "Isolation of Organic Water Pollutants by XAD Resins and Carbon," *Journal of Chromatography*, Vol. 150, pp. 381-392, 1978.
15. D. K. Basu and J. Saxena, "Monitoring of Polynuclear Aromatic Compounds in Water II. Extraction and Recovery of Six Representative Compounds With Polyurethane Foams," *Environmental Science and Technology*, Vol. 12, pp. 791-795, 1978.
16. J. Navratil, R. Sievers, and H. Walton, "Open-Pore Polyurethane Columns for Collection and Preconcentration of Polynuclear Aromatic Hydrocarbons from Water," *Analytical Chemistry*, Vol. 49, No. 14, pp. 2260-2263, 1977.
17. M. Chasanov, R. Kunin, and F. McGarvey, "Sorption of Phenols by Anion Exchange Resins," Industrial and Engineering Chemistry, Vol. 48, No. 2, pp. 305-309, 1956.
18. B. Kim, V. Snoeyink, and F. Saunders, "Adsorption of Organic Compounds by Synthetic Resins," *J. WPCF*, Vol. 48, No. 1, pp. 120-133, 1976.
19. Z. A. Grosser, J. C. Harris, and P. L. Levins, "Quantitative Extraction of Polycyclic Aromatic Hydrocarbons and Other Hazardous Organic Species From Process Streams Using Macroreticular Resins," presented at the 3rd International Symposium on Polynuclear Aromatic Hydrocarbons, October 1978.

MEASUREMENT OF COLOR IN TEXTILE DYEING WASTEWATERS

Linda W. Little*

Abstract

All presently accepted "standard methods" for determining color of water and wastewaters are based on spectrophotometric analysis. The standard American Public Health Association determination of color, initially designed for application to natural waters, is based on comparison of true (soluble) color of the test sample to known concentrations of yellow-brown color. Since even slight amounts of turbidity interfere with spectral analysis, turbid samples require filtration prior to analysis. Application of the methods to textile dyeing wastewater is complicated due to the presence in many of these wastewaters of insoluble dyes and dyes of hues substantially different from the yellow-brown color of natural waters. Recent approaches to modification of standard methods to improve applicability to all hues [American Dye Manufacturers's Institute (AMDI) Method] and for improved and simplified calculation of color values (CIELAB, CIELUV) will be discussed, as well as possible approaches to obtaining realistic color values for wastewaters containing dispersed dyes and other dyes that are removed by filtration.

The presently accepted standard methods for determination of color in water and wastewater were developed for potable, surface, and other natural waters in which the color is generally soluble and yellow-brown in hue. In the standard American Public Health Association (APHA) procedure, "true color" is defined as "the color of water from which the turbidity has been removed," and "apparent color" as the "color due to substances in solution, but also that are due to suspended matter." (ref. 1) Apparent color is determined on the sample without prior filtration or centrifugation. In practice, the reported color value is generally the true or soluble color.

Accurate color determinations of effluents from textile and carpet dyeing are complicated by two factors: (1) the colors may be drastically different from the yellow-brown hue to which the APHA value is related and (2) the color components may be insoluble in aqueous media.

To overcome the first problem, members of the American Dye Manufacturers Institute (ADMI) have developed a modified color method that is an extension of the APHA method and that is "(1) applicable to any hue, (2) sensitive to small color differences, (3) related to APHA values, and (4) requires relatively inexpensive instrumentation" (ref. 2). This method has now been adopted by EPA (ref. 3) and is under consideration for the 15th edition of *Standard Methods for the Examination of Water and Wastewater.*

THE ADMI COLOR METHOD (ref. 2)

As stated above, the ADMI measurement was designed to be an extension of the APHA color method. As such, the color is defined as soluble color and the samples must be prefiltered through a celite-coated filter crucible or celite-coated glass fiber filter paper. Such filtration will obviously remove particulate color and may also remove certain dyes through adsorption. In brief, the ADMI method involves:

- prefiltration to remove insoluble materials,
- determination of tristimulus values with the aid of a spectrophotometer or a tristimulus colorimeter,
- conversion of the tristimulus values to corresponding Munsell values by use of appropriate tables or by calculation,
- calculation of the value DE, (the Adams-Nickerson Color Difference related to a definition of the color space designed as ANLAB), and
- conversion of DE to the ADMI value by calculation.

---

*Chemistry and Life Sciences Division, Research Triangle Institute, Research Triangle Park, NC.

A variety of spectrophotometric equipment can be used, ranging from a relatively inexpensive colorimeter especially designed for the procedure to a "double beam recording spectrophotometer coupled to a digital computer (which) will eliminate calculation time and generate ADMI values within a matter of seconds" (ref. 2). Without the aid of tables and of programmable calculators or computers, the calcultions are extremely tedious.

The ADMI procedure has been subjected to interlaboratory testing and a sample having a color value of 100 units has been shown to have a 95 percent confidence limit of less than ± 5 units.

CONCEPT OF COLOR SPACE

As noted above, the ADMI procedure is based on a color difference formula devised by Adams and Nickerson and recommended by the Society of Dyers and Colorists in 1970. This formula is defined as the difference "between any two specimens...as the distance between their positions in the uniform colour space known as ANLAB" (ref. 4). The Adams-Nickerson formula is quite complex, involving a fifth-degree polynomial equation to quantify the relationship between one of the three tristimulus values and the Munsell value.

At this point, it may be appropriate to briefly discuss the notion of color space, a very complex concept accompanied by very complex mathematical representations. The human eye responds differently to various hues and brightnesses. In the ideal color space representation, one unit of color difference at any one area of the color space (e.g., in the yellow area) would be exactly equal to one unit in any other area (e.g., in the blue area). Therefore, a blue solution of 100 color units would have the same color depth as a yellow solution of 100 color units. The color space is 3-dimensional and nonspherical. A given color can be accurately defined, or located in the color space, by three primary or tristimulus values, providing these values are properly weighted in the calculation. In practice, the three tristimulus values correspond to standard red, blue, and green filters. A relatively simple explanation of the nature of color, accompanied by full color diagrams, may be found in reference 5. Suffice it to say that a multitude of mathematical formulae have been devised to define the color space.

The international authority for all aspects of color is the Commission Internationale de l'Eclairage (CIE). This organization has valiantly attempted unification of the variety of different evaluation practices in the hopes of coming up with "a single uniform color-space and color-difference formula...which will serve most industry applications satisfactorily" (ref. 6). The two most promising practices at the present time are: (1) a color difference formula based on uniform color spaces as defined by CIE in 1964 and designated as CIELUV, and (2) a cube root version of the Adams-Nickerson color difference formula designated as CIELAB. The latter has found more favor with the textile and dyestuff industries. The ADMI procedure can be modified to incorporate the simplified CIELAB formula, thus greatly simplifying calculation of color values. Detailed discussions of the CIELAB may be found in articles by McLaren and associates (refs. 4,7). Other detailed discussions of color measurement in the textile industry are included in proceedings of a recent AATCC workshop/seminar (ref. 8).

APPLICATION OF COLOR MEASUREMENT PROCEDURES TO ACTUAL WASTEWATERS

We have, then, a variety of ways to obtain a number representing "color" of waters and wastewaters. But what is the significance of the measurement we have obtained? How does this measurement, however precise and reproducible, relate to the basic question: How much color is leaving the effluent from the dyeing operation and entering into the receiving stream? Given this concern, one is forced to question the relationship between the effluent and the sample that is actually subjected to analysis, i.e., the portion of the effluent that is capable of passing through a celite filter. During extensive research on the characterization, bioassay, and treatability of dyes and dyeing wastewaters (refs. 9 through 13), we observed that with certain wastewaters, such as those from disperse dyeings, measurement of either true color or apparent color failed to adequately represent the color intensity obvious to the eye. It appeared that the discrepancy was due to (1) interference by turbidity, especially noncolored suspended solids, in the apparent color determination; and (2) removal of most of the color in the prefiltration step of the true color determination. Preliminary research on several synthetic dyeing wastewaters (i.e., those prepared in the laboratory with disperse dyes and dispersants) substantiated the removal of most of the color by such processes as membrane filtration, diatomite filtration, glass fiber filtration, and centrifugation (ref. 14). Obviously the true color bears little resemblance to the real color of the effluent unless the effluent has been subjected to pretreatment to give color removals equivalent to these processes.

The study just described also revealed that with disperse dyeing mixtures, addition of organic solvents such as acetone prior to the filtration step would facilitate measurement of most of the color. Much additional testing with a variety of solvents, dyes, and dyeing wastewaters will be required to determine the optimum conditions for measurement of color. The first criticism is apt to be that addition of solvent will lead to the overestimation of color in the effluent and that unrealistic requirements for color removal will thereby result.

SUMMARY

At the present time there is not a perfect or even a reasonably good method for accurately estimating the total color of complex wastewaters containing undissolved dyes. The challenge facing us is development of an accurate method that can be readily performed by wastewater operators or by monitoring personnel, preferably with moderately priced equipment. Two approaches to such a method are modification of the existing procedures for color analysis (for example, by solvent addition) or development of new procedures that measure color in either the soluble or insoluble state. The ultimate goal of either approach will be the development of a method that gives a realistic estimate of color in actual effluents from textile and dyeing operations.

REFERENCES

1. American Public Health Association, American Water Works Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater,* 14th ed., Method 204, "Color," American Public Health Association, Washington, DC, 1976.
2. W. Allen, et al., "Determination of Color of Water and Wastewater by Means of ADMI Color Values," Proceedings, 28th Industrial Waste Conference at Purdue University, *Engineering Bulletin of Purdue University,* Engineering Extension Series No. 142, p. 661, 1973.
3. U.S. Environmental Protection Agency, *Methods for Chemical Analysis of Water and Waste,* addendum, "Color (ADMI units)," Storet Nos. 0082 and 0083, Environmental Protection Agency, Office of Technology Transfer, Washington, DC, undated.
4. K. McLaren and B. Rigg, "XII—The SDC Recommended Colour-Difference Formula: Change to CIELAB," *Jour. Soc. Dyers and Colorists,* Vol. 92, p. 337, 1976.
5. M. M. Lih, "Color Technology," *Chem. Engng.,* August 12, 1968.
6. Commission Internationale de l'Eclairage, *Official Recommendations of Uniform Color Spaces, Color-Difference Equations, Metric Color Term,* Supplement No. 2 to CIE Publication No. 15, *Colorimetry* (E-1.3.1) 1971, 19 pp., 1976.
7. K. McLaren, "XIII—The Development of the CIE 1976 ($L^*a^*b^*$) Uniform Colour Space and Colour-Difference Formula," *Jour. Soc. Dyers and Colorists,* Vol. 92, p. 338, 1976.
8. AATCC, *Color Measurement in the Textile Industry,* American Association of Textile Chemists and Colorists, Research Triangle Park, NC, 1977.
9. L. W. Little and J. C. Lamb III, "Acute Toxicity of 46 Selected Dyes to the Fathead Minnow, *Pimephales promelas,*" *Dyes and the Environment,* American Dye Manufacturers Institute, Inc., NY, 1973.

10. L. W. Little, J. C. Lamb III, M. A. Chillingworth, and W. B. Durkin, "Acute Toxicity of Selected Commercial Dyes to the Fathead Minnow and Evaluation of Biological Treatment for Reduction of Toxicity," Proceedings of the 29th Industrial Waste Conference, *Engineering Bulletin of Purdue University*, Engineering Extension Series No. 145, p. 524, 1974.
11. J. W. Ericson and L. W. Little, "Applicability of ATP Measurements for Determination of Dye Toxicity in Short Term Algal Assays," *J. Elisha Mitchell Scientific Soc.*, Vol. 92, No. 2, 1976.
12. L. W. Little, and J. W. Ericson, "Biological Treatability of Wastewaters from Textile and Carpet Dyeing Processes," Proceedings of the 8th Mid-Atlantic Industrial Waste Conference, January 12, 1976, Newark, DE, pp. 201-216.
13. T. Crowe, C. R. O'Melia, and L. Little, "The Coagulation of Disperse Dyes," *Proceedings of the 32nd Purdue Industrial Waste Conference* (May 1977), Ann Arbor Science, Ann Arbor, MI, pp. 655-662, 1978.
14. R. Goodman, "Evaluation of the ADMI Procedure for Measuring Color in Textile Dyeing Wastewater, Master's report (under the direction of L. W. Little), Department of Environmental Sciences & Engineering, University of North Carolina, Chapel Hill, NC, 1977.

USE OF BIOASSAY SCREENING TECHNIQUES FOR NPDES* PERMITS

W. H. Peltier, L. B. Tebo, Jr.[†]

Abstract

Effluents limits placed in the NPDES permits do not take into account the presence of byproducts, degradation compounds, unreported compounds, the synergistic action of these compounds, nor receiving water characteristics in the control of toxicity to aquatic organisms. In order to evaluate the toxicity of complex effluents being discharged to freshwater and saltwater environs, EPA Region IV is including, in selected NPDES permits, a bioassay screening requirement. This requirement is in the form of periodic 24-h acute static toxicity tests which result in a pass or fail criteria. The criteria are based on 50 percent survival of selected standard test organisms exposed to a single percent effluent volume. Failure to meet the criteria results in requiring the permittee to conduct additional studies such as: acute and/or chronic flowthrough toxicity testing, receiving water biological monitoring, bioaccumulation studies, wastewater persistence studies, flavor impairment, and avoidance studies. The bioassay screening requirement is not intended to replace the traditionally required parameters in a permit such as BOD, COD, and chemical-by-chemical limitations, but is an additional compliance parameter.

One of the goals of the 1977 Clean Water Act states that, "it is a national policy that the discharge of toxic pollutants in toxic amounts be prohibited." Historically in Region IV, the U.S. Environmental Protection Agency (EPA) has been conducting bioassays at facilities discharging complex wastewater to a receiving water. These bioassays were conducted to evaluate the lethality of complex wastewater discharges to selected aquatic organisms.

Present EPA regulatory programs to control the discharge of toxic wastewaters emphasize specific limits on individual chemicals. For chemicals of known toxicity and for which economical methods of identification and quantification are available, the specific chemical limit is unquestionably a most efficient approach.

Unfortunately, the individual chemical approach provides no control of the tens-of-thousands of chemicals for which toxicity data are lacking or inadequate and chemical characterization techniques are unavailable or prohibitively expensive. The individual chemical approach also provides little means for controlling the toxicity of wastewater discharges where toxicity is a function of the mixture of chemicals in the wastewater. In this situation, toxicity testing must be used to control the discharge of toxicants.

A measure of the lethality problem of complex wastewater discharges is indicated by Region IV's experience with 64 onsite 96-h flow-through toxicity tests where 49 of the discharges were lethal to selected aquatic organisms. Twenty-seven of fifty complex wastewater discharges tested at the EPA Athens, Georgia laboratory using 96-h static toxicity tests were lethal.

The chemical analyses of many of the wastewaters tested for toxicity disclosed the inadequacies of the chemical by chemical approach in protecting the aquatic community. Up to 50 unpermitted chemicals have been detected in a single wastewater source being discharged to the receiving water. Of course, many of these chemicals were byproducts on degradation products of which very little is known regarding their toxicity.

It is apparent that regulatory agencies must have a means of controlling the discharge of toxic complex wastewaters and the innumerable pollutants of unknown toxicity. The most direct approach to this problem is establishment of limits based on the response of aquatic organisms to potentially toxic wastewater discharges. Therefore, EPA is developing a program for the second round of NPDES permitting whereby toxicity limits based on the lethality of the wastewater to aquatic organisms is made a part of the NPDES permit. The permittee would be required to conduct toxicity screening tests at the wastewater concentration (percent wastewater) specified as a toxicity limit in the permit.

---

*National Pollutant Discharge Elimination System.

[†] U.S. EPA, Region IV, Surveillance and Analysis Division, Athens, GA.

The screening test would be based on a single wastewater concentration utilizing 24-h acute static tests. A monthly testing frequency would be required using a selected test organism. The selected organisms would be based on whether the wastewater is freshwater or saltwater. If the wastewater is fresh, then either the fathead minnow *(Pimephales promelas)* or water flea *(Daphnia magna* or *pulex)* will be used. On the other hand, if the wastewater is saltwater, then either the sheepshead minnow *(Cyprinidon variegatus)* or mysid shrimp *(Mysidopsis* sp.) would be used as the test organism. The protocol for the screening test is in the EPA publication ***Methods for Measuring the Acute Toxicity of Effluents to Aquatic Organisms*** (ref. 1).

The toxicity limit calculation for the single test concentration is based on the following formula:

$$LC_{50}{}^{\ddagger} \geqq \frac{WC}{AF^{\S}}$$

where:

LC_{50} = the concentration (expressed as percent) at which the wastewater is lethal to 50 percent of the test organisms,

WC = receiving water wastewater concentration (expressed as percent) at the 7Q10 flow in a river, or for a lake or estuary, the concentration at the boundary of the mixing zone, and

AF = numerical value which, when applied to acutely toxic concentration (LC_{50}) will result in a safe concentration.

Example 1 - Wastewater discharged to a river via a diffuser system to promote rapid mixing.

Data required by permit writer are as follows:

Mean daily wastewater flow = 2 mgd
7Q10 = 270 mgd
Application factor = 0.01 for a persistent wastewater.

Toxicity limit:

$$LC_{50} \geqq \frac{\frac{QW}{QW + QR} \times 100}{AF}$$

$$LC_{50} \geqq \frac{\frac{2}{2 + 270} \times 100}{0.01}$$

$$\geqq 74 \text{ percent.}$$

Thus, in conducting the screening test, the permittee would use 74 percent wastewater by volume and 26 percent dilution water.

Example 2 - Wastewater discharged to a lake or estuary via a diffuser system to promote rapid mixing.

Data required by permit writer is as follows:

- Permittee is required to display on a map isopleths of wastewater concentrations occurring in the receiving water (Figure 1).
- Numbers of hectares within each isopleth.
- Ecologically and economically important resources in the receiving water are to be identified for each isopleth.
- Application factor to be used for persistent wastewater is 0.01.

Toxicity limit:

$$LC_{50} \geqq \frac{\text{mixing zone boundary}}{0.01}$$

$$LC_{50} \geqq \frac{0.25}{0.01} \geqq 25 \text{ percent.}$$

Thus, in conducting the screening test the permittee would use 25 percent wastewater by volume and 75 percent dilution water.

Failure of a screening test must be reported in writing within 5 working days after the test

---

[‡] If the result of this calculation exceeds 100 percent for a river, then the screening toxicity test must be conducted on undiluted (100 percent) wastewater with a 90 percent or greater survival rate required of the test organisms.

[§] If the permittee can demonstrate that the wastewater toxicity is not persistent and/or bioaccumulative in the environment, then an application factor of 0.05 can be used, otherwise an application factor of 0.01 is utilized in the formula.

is completed. Within 90 days after any test that caused a lethality of 50 percent or more, the permittee must develop and submit to EPA Region IV a plan and schedule for reducing the toxicity of the wastewater to a safe level. Once the toxicity is reduced to the NPDES permit toxicity limit, a return to the monthly screening toxicity tests are to be initiated.

In summary, the screening toxicity test described in this paper is an additional approach being used by EPA Region IV in the issuance of second round NPDES permits. Both specific limits on known toxic chemicals as well as screening toxicity tests will be used to control toxicants discharged into our receiving waters.

REFERENCE

1. U.S. Environmental Protection Agency, *Methods for Measuring the Acute Toxicity of Effluents to Aquatic Organisms,* U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, EPA 600/4-78-012, p. 52, 1978.

Session VI: ENERGY AND MATERIALS CONSERVATION

John R. Rossmeissl, Session Chairman

Preceding page blank

RECLAMATION OF WARP SIZES USING THERMAL PRECIPITATION

Warren S. Perkins, Robert P. Walker, Leo J. Hirth*

Abstract

A novel method for size reclamation based on precipitation of the size material by heating the desize washwater is reported. The method uses hydroxypropylatedcellulose (HPC), which is soluble in cool water but insoluble in warm water. Separation of the thermally precipitated hydroxypropylcellulose from water is discussed along with the applicability of the HPC as a warp size and the economics of the process.

INTRODUCTION

Size materials constitute a major portion of the biochemical oxygen demand (BOD) and dissolved solids in the wastewater from woven fabrics finishing processes. The BOD contributed by desizing starch-sized fabrics may be 45 percent or more of the BOD load from the finishing plant. The BOD load from desizing may be lowered by using synthetic sizing polymers such as polyvinyl alcohol (PVA) or carboxymethylcellulose (CMC) either alone or in mixtures with starch. However, these synthetic polymers do not easily biodegrade and remain dissolved in the finishing plant wastewater.

A process to recover and recycle warp sizes probably has the potential to lower the BOD, COD, and dissolved solids in textile finishing plant effluents more than any other single change in textile processing. Such processes have been the subject of much research and development work in recent years. The following are specific examples of approaches to size reclamation:

- Reclamation of carboxymethylcellulose by chemical precipitation from the desize wastewater has been studied but not commercialized.
- Recovery of polyvinyl alcohol by chemical precipitation has also been subject to investigation.
- Studies of recovery of warp sizes using solvent sizing and desizing have been made, and a solvent sizing and desizing system has been developed by two Italian machinery companies.
- Recovery of PVA by ultrafiltration of the desize wastewater is now being done commercially.

The tremendous interest of the U.S. Textile Industry in the reclamation of warp sizes is understandable since the economic outlook for such a development is as favorable as are the environmental considerations. The size material adds no value to the fabric. It is applied to the yarn in slashing to improve the efficiency with which the yarn can be woven into fabric. It is normally removed in desizing and disposed of in a wastewater treatment facility. Therefore, the size material itself adds to the cost of fabric production. A process for reclamation of the size material would prove profitable to the textile mill if the cost of reclaimed size is lower than that of virgin size.

PRINCIPLE OF SIZE RECLAMATION USING THERMAL PRECIPITATION

The size reclamation process that is the subject of this paper uses a size selected from a group of polymers having the unusual property of being soluble in water at room temperature but insoluble in water at some higher temperature. Hydroxypropylcellulose (HPC), on which most of the research work at Auburn has been based, is such a polymer. HPC, which is soluble in water at room temperature, becomes almost completely insoluble in water above about 45° C. Therefore, precipitation of HPC from desize wastewater can be accomplished by merely heating the desize wastewater to above 45° C. A schematic diagram of the desizing and recovery system being studied is shown in Figure 1. Washing of the HPC from the fabric takes place in water at a temperature below 40° C. The desize water containing HPC at a

---

*Department of Textile Engineering, Auburn University, Auburn, AL.

Preceding page blank

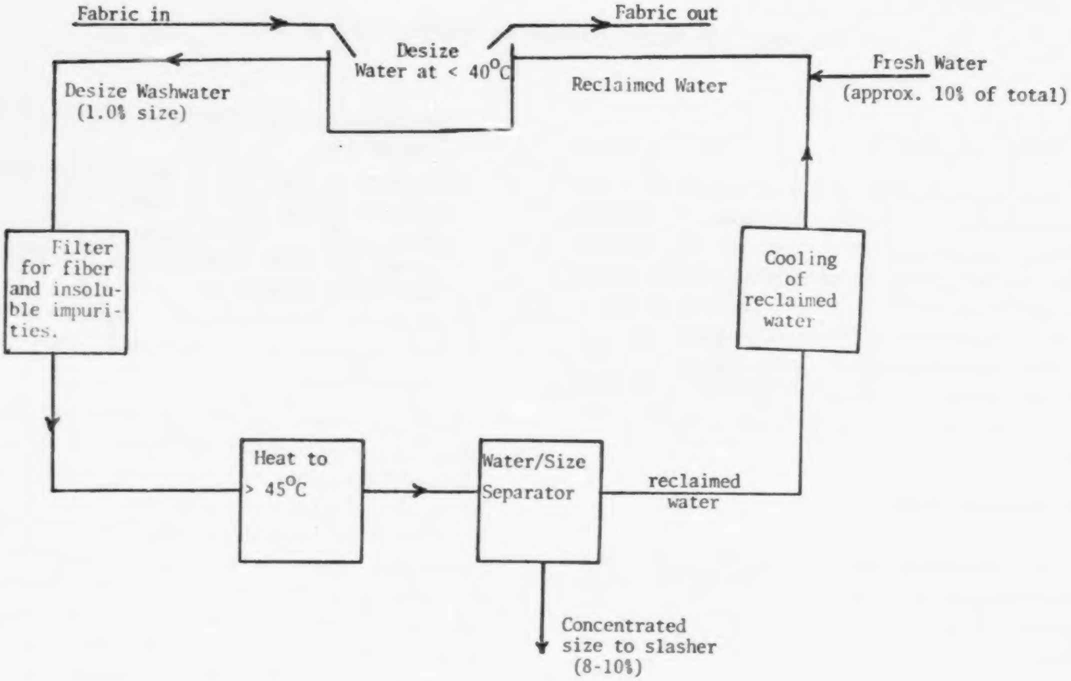

Fabric in
Fabric out
Desize
Water at < 40°C
Desize Washwater
(1.0% size)
Reclaimed Water
Fresh Water
(approx. 10% of total)
Filter for fiber and insoluble impurities.
Cooling of reclaimed water
Heat to > 45°C
Water/Size Separator
reclaimed water
Concentrated size to slasher (8-10%)

Figure 1. Schematic of desize and recovery system.

concentration of 0.5 to 1.5 percent is filtered to remove insoluble impurities and heated to above 45° C to precipitate the HPC. The precipitated HPC is then separated from most of the water. The HPC redissolves when cooled to yield a solution that can be reused in slashing. The recovered water can be cooled to below 40° C and reused in the desize washer. Hydroxypropylmethylcellulose (HPMC) also exhibits the thermal precipitation phenomenon and can be used in the process.

DESIGN OF WATER/HPC SEPARATOR

The heart of the reclamation system being studied is the separation of the precipitated particles of HPC from most of the water to obtain a size solution of sufficient concentration to reuse in slashing. Separation of the precipitated HPC by filtration and centrifugation have each appeared feasible in the laboratory. However, the most promising separation technique tested was settling by gravity.

Thermally precipitated HPC separates from water as a colloidal dispersion. The HPC particles have a negative zeta potential and can be made to coagulate and settle rapidly by adding a cationic agent. A variety of these settling assistants were tested for their benefit to the HPC recovery process. Ions such as Na^+, CA^{+2}, and Al^{+3} cause thermally precipitated HPC particles to coagulate and settle rapidly. The coagulating effect increases with higher cationic charge and with increase in concentration of cations in the concentration ranges used in this work. Cationic polyelectrolytes may also be used to enhance the settling of HPC particles in water. The most useful settling assistant used in this work was aluminum sulfate. One-half to one percent aluminum sulfate based on the weight of the HPC is sufficient to cause rapid settling of thermally precipitated HPC in water. This level of aluminum sulfate does not affect the solubility of HPC in water. When the water temperature is below 45° C the HPC is readily soluble in water containing

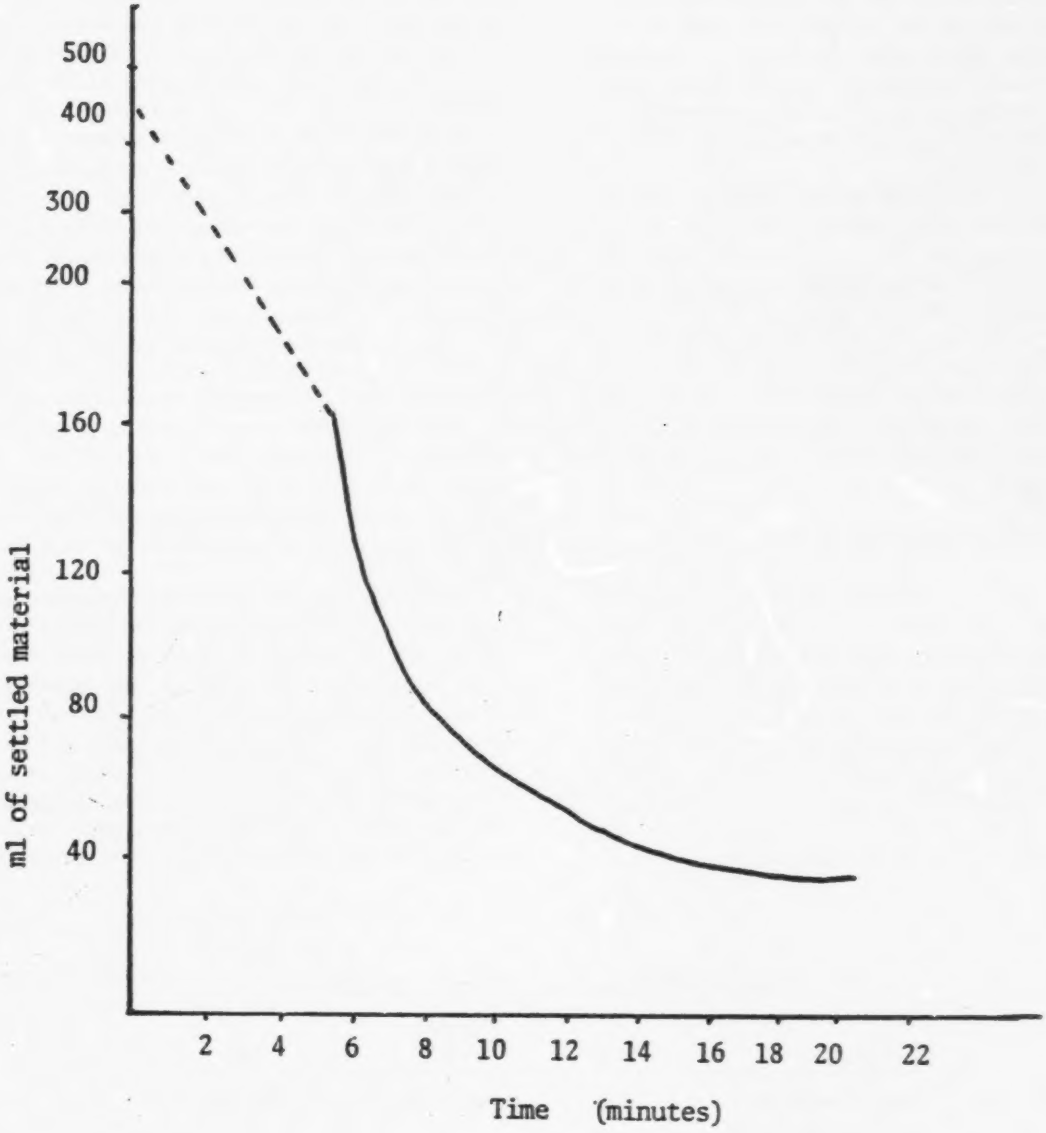


Figure 2. Settling rate of precipitated HPC at 50° C.

1 percent aluminum sulfate on the weight of the HPC. Analysis of the recovered HPC (concentrate) and the recovered water revealed that the aluminum ions concentrated themselves in the recovered HPC. That is, the aluminum ions become a part of the reclaimed HPC solution and addition of aluminum to the desize washwater is necessary only when virgin HPC is used. Several cycles of use and reclamation of HPC can be run without any additions of aluminum sulfate after the initial run. Studies of physical properties of films of HPC revealed that 1 percent by weight of aluminum sulfate in the HPC caused no deterioration of properties of the material.

Figure 2 illustrates the settling rate of precipitated HPC in water. The volume of the test solution was 450 ml and it contained 4.5 g of HPC and 0.030 g of aluminum sulfate. In 15 to 20 minutes virtually all of the HPC had settled into the bottom 45 ml of the container, a 500-ml graduated cylinder. Experiments of this type have yielded solutions containing up to 30 percent by weight of reclaimed HPC at typical recovery levels of 85 to 95 percent of the HPC in the desize washwater.

UTILITY OF HPC FOR SIZING

The economic success of a textile greige mill depends to a large degree on the efficiency with which yarns may be woven into fabric. Therefore, the performance of the size material in protecting the yarn is of utmost importance. Since HPC has not previously been used as a warp size, an important aspect of the work that is being done at Auburn is the evaluation of the performance of HPC as a warp size. Three types of studies regarding the performance of HPC as a warp size are in progress. They are:

1. Properties of films of HPC.
2. Properties of yarns sized with HPC.
3. Weaving performance.

The primary (and sometimes only) ingredient in a size formulation is a film-forming agent. Studies of size materials in the form of films allows evaluation of the effect of various additives and contaminants on material properties that may affect performance of the size material. Tensile strength and elongation of films of HPC, PVA, and CMC are compared in Table 1. The strength of HPC is similar to that of CMC, which is considerably lower than that of PVA. However, the strength of HPC is adequate for warp sizing. PVA is sometimes considered too strong for fine yarns and can cause problems if it does not split easily enough at the slasher lease rods. The elongation of films of HPC is intermediate between that of CMC and PVA, both of which are successfully used as warp sizes. Other properties of HPC such as adhesion to various fibers; resolubility in water during desizing; and stability to mechanical action, chemical action, and moderate heat in use appear to be adequate for the reclamation process.

Typical results of tests of properties of yarns sized with HPC are shown in Table 2 and compared to properties of yarns sized with PVA. The effect of HPC on the breaking strength and elongation of the polyester/cotton yarns was about the same as the effect of PVA. The elongation of the sized yarns was about 2 to 3 percent lower than that of unsized yarns. The strength of the yarns increased by about 15 percent as a result of sizing with either PVA

TABLE 1. PROPERTIES OF HPC*, CMC† and PVA‡

Property	Materials		
	PVA	HPC	CMC
Tensile strength (psi)	3,100	800-1,300	1,000-1,500
Elongation at break (%)	200	75	7

*Hercules, Inc., Klucel J.

†Hercules, Inc., Warp Size Grade CMC.

‡Du Pont, Elvanol T-25.

TABLE 2. PROPERTIES OF 36/1, 50/50 POLYESTER/COTTON YARNS SIZED WITH PVA OR HPC

Sample description	Size concentration in formulation	Break factor (oz. × counts)	Elongation (%)	Abrasion Resistance (#cycles)
Unsized control	--	432	13.4	20
PVA with lubricant	10	500	10.7	2,000+
HPC	10	501	11.0	1,200

or HPC. The abrasion resistance of the yarns improved drastically as a result of sizing with HPC or PVA. These yarns must withstand at least 300 to 400 abrasion cycles to be weaveable. The physical properties of yarns sized with HPC are adequate for weaving loosely constructed fabrics, but the abrasion resistance is borderline for tightly constructed fabrics such as sheeting.

ECONOMICS OF SIZE RECLAMATION

Estimates of the economics of reclaiming HPC are shown in Table 3. These figures are based on settling the HPC in large tanks. Also shown are cost figures on an ultrafiltration system for PVA recovery and some costs for use of conventional desizing followed by wastewater treatment.

The initial capital investment for an ultrafiltration reclamation system for 272,232 kg (600,000 pounds) of fabric per week is estimated to be $805,000 while that for a thermal precipitation system is $262,600. Annual operating costs including labor, utilities, insurance, taxes, maintenance materials, and depreciation total $249,500 for ultrafiltration and $82,850 for thermal precipitation. The cost of energy for running a thermal precipitation recovery system will be about $54,000 per year less than that required for a conventional desize process or an ultrafiltration system because of lower water temperature requirements. The cost of size for a thermal precipitation system is $507,500 annually, considerably higher than the $460,000 for a conventional system and the $252,000 for an ultrafiltration system using PVA. Total annual operating costs for a ther-

TABLE 3. ECONOMICS OF SIZE RECLAMATION (BASIS IS 600,000 POUNDS OF FABRIC PER WEEK)

	Ultrafiltration	Thermal percipitation	Conventional
Initial capital investment	$805,000	$262,600	--
Annual operating costs*	249,500	82,850	--
Energy for hot water	75,000	21,000	75,000
Size materials	252,000†	507,500‡	460,000
Wastewater treatment§	20,000	14,000	198,000
Total annual operating costs	$596,500	$625,350	$733,000

*Excluding size material costs, cost of energy for hot water and cost of wastewater treatment.

†Based on 20 percent loss of PVA.

‡Based on 15 percent loss of HPC.

§Estimated for 1983.

mal precipitation system are estimated to be slightly higher than for ultrafiltration but less than conventional desizing systems.

ACKNOWLEDGMENT

The work reported in this paper was performed under the partial sponsorship of the U.S. Environmental Protection Agency through Grant No. R 805128-010. The work was performed by the Auburn University Department of Textile Engineering in cooperation with Alabama Textile Education Foundation through the Auburn University Water Resources Research Institute with assistance from the Auburn University Engineering Experiment Station. This paper covers work completed by August 31, 1978. The project is scheduled for completion by December 20, 1979.

AN INDUSTRIAL WASTEWATER RECIRCULATION SYSTEM FOR THE FIBROUS GLASS TEXTILE INDUSTRY

S. H. Thomas, D. R. Walch*

Abstract

In this presentation the concept, development, and installation of an industrial wastewater recirculation system for the fibrous glass textile industry will be addressed.

INTRODUCTION

For those not familiar with fibrous glass processes and products, I'll briefly describe them. At Owens-Corning Fiberglas facilities, the process begins with the mixing and feeding of raw batch to a furnace. Furnaces for textile processes are either gas- or oil-fired and are of the regenerative or recuperative type. The molten glass from any of the furnaces drains into a forehearth and through a bushing. Bushings are of a platinum material with a number of orifices in various sizes to satisfy the end product. The fibers have either binders or sizes applied and are then cured. The final products of our process include fibrous glass in forms for further manufacture, fabrication, or in many instances, for finished product.

Owens-Corning, product-wise, is essentially divided into four categories: textile, insulation, roofing, and special products. Owens-Corning manufactures everything from a fiber one-tenth of one-thousandth of an inch in diameter, to bathtubs and huge underground gasoline storage tanks, to the new 105-acre Fiberglas fabric roof for the Haj Terminal at the Jeddah International Airport in Saudia Arabia. However, this report will be limited to discussion of textile products as manufactured at our Anderson, South Carolina, facility.

To start my story, I will have to take you back 20 years to 1958 when I first started to work with Owens-Corning Fiberglas and the industrial wastewater systems of that era. Like most other industries of that time, we were busy trying to treat industrial wastewater for suitable discharge. My first industrial wastewater problem was finding a suitable manner to discharge approximately 4,000 gallons per minute of process water with a high BOD and COD, and with suspended solids and phenol in concentrations of up to 600 ppm from an insulation facility.

The first step was to look for methods of treatment available. At that time little was known about the treatment of phenols and no information was available from any fibrous glass facilities either in the United States or throughout the world. We started from scratch using the famous old method of trial and error. By 1960 I had developed an extended aeration system for the degradation of the phenol as well as the other parameters listed. Phenols could be reduced from 1,000 ppm to about 2 ppm, which was a safe limit for fish as determined by bioassay tests. I recognized at this time that this system would provide me with about 10 years of breathing room before finding alternate methods to further reduce the discharge of contaminants into the waterways of our nation. In that same year, 1960, I also inherited the four textile operations in the company. It might be of interest at this point to mention that in 1960 Owens-Corning had nine operating facilities in seven States. Today we have 90 facilities in 27 States.

Listening to the thoughts and ideas being mentioned at that time in Washington, DC, and State capitols convinced me that all our initiative should be directed toward total recirculation of all industrial wastewater within our corporation. It was an idealistic goal, but it was worth a desperate effort. The benefits at that time seemed justifiable and, of course, today are stupendous.

The textile industrial wastewater treatment systems of that era consisted of primary and secondary systems for the combined sanitary and industrial wastewater. These systems adequately reduced the contaminants for safe discharge to waterways. At this time, we were using starch sizes for our textile products; this was many years before we started using exotic chemicals for sizes to meet product uses and qualifications.

---

*Owens-Corning Fiberglas Corporation, Toledo, OH.

Being more familiar with the insulation products' wastewater from previous work, this appeared to be the area of greatest concern in the future. I directed my attention to improving the insulation products' wastewater systems. With this strong urge and my own headstrongness, I quietly developed an initial concept for a totally recycled system.

In the next 8 years I had to listen to the "No, it won't work," etc., etc., but continually tried to find answers and ways around the ever-rising problems. By 1968, we turned the valves and started our first totally recycled industrial wastewater system at Barrington, New Jersey. I might add at this point that during these trying years top-level management was behind me, helping wherever necessary.

In 1969, modifications were made to two other insulation facilities in Texas and Georgia, and these facilities converted to totally recirculated industrial wastewater systems (See Figure 1). One new facility has been added since then and it too is on total recycle, as will all other new facilities of this type in the future. Our record on insulation facilities as of today is five plants on total recycle and two more under construction, both to be on recycle systems by 1980.

With the taste of success at our insulation plants, we directed our attention to the textile facilities. The first step for any process to be adaptable to a totally recycled system is to convince management, and particularly plant management, that you can develop the concept into a workable system, with the necesssary justification. Once this is accomplished, all other steps are left completely up to the technical competence of the team working on the

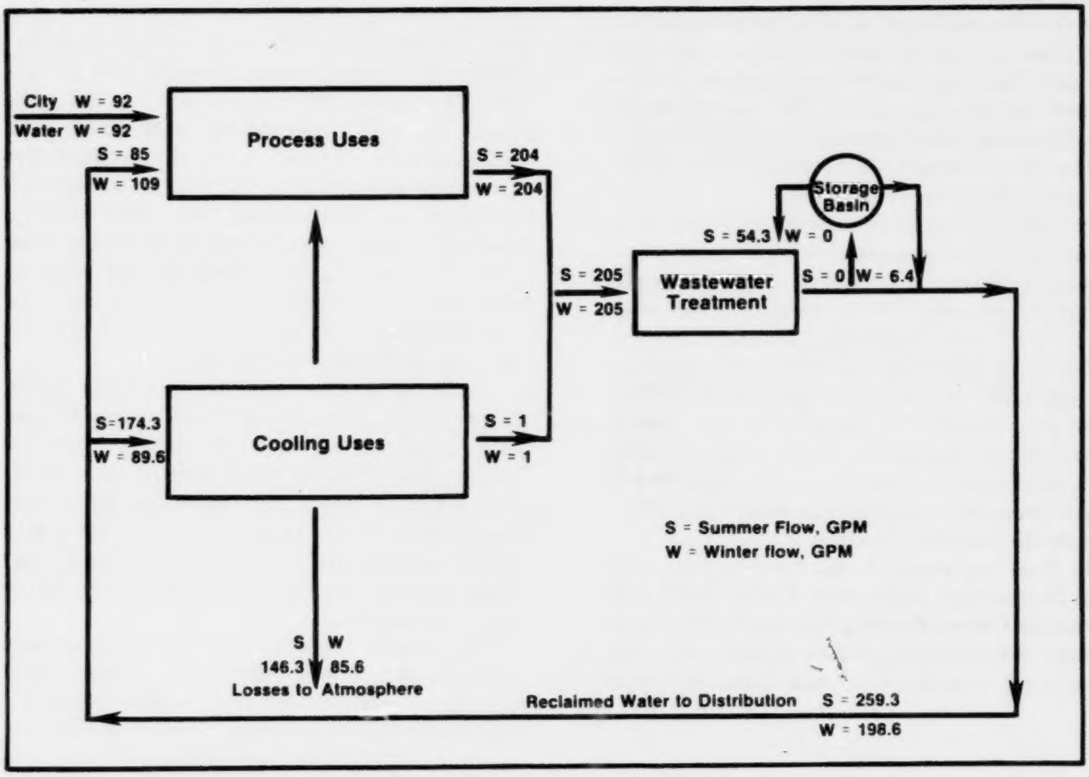

City W = 92
Water W = 92
S = 85
W = 109
Process Uses
S = 204
W = 204
Storage Basin
S = 54.3
W = 0
S = 205
W = 205
Wastewater Treatment
S = 0
W = 6.4
S=174.3
W = 89.6
Cooling Uses
S = 1
W = 1
S = Summer Flow, GPM
W = Winter flow, GPM
S
W
146.3
85.6
Losses to Atmosphere
Reclaimed Water to Distribution
S = 259.3
W = 198.6

Figure1. Overall water balance for recirculation.

project. The second step is to reduce any and all waste flows at the facility so that the demand for water is greater than the discharge. In the case of the Anderson textile facility, it was necessary to devise piggyback systems, or higher quality water usage discharged to lower quality water usage systems, before final discharge to the treatment facilities.

Once the demand and supply balance had been established, it was necessary to analyze the final effluent as well as determine the parameters required for water usage in the various systems. This is a very crucial phase since complex facilities have discharges where the parameters can vary frequently. Usually a long-term sampling program is required to establish the basis for treatment as well as reuse. Generally there are one or more systems that have more critical requirements for treatment than all others. At Anderson one such system existed.

At the Anderson facility it was found necessary and desirable to develop the treatment required to satisfy this system, then design a small pilot trial including actual use of the field conditions to provide a more reliable system. At Anderson the critical water usage system was the cooling of a heat exchanger which in turn cooled the glass fibers as they were formed (See Figure 2). The temperature of the glass fibers at the tip of the heat exchangers is approximately 1,800° F. This must be significantly reduced before the sizing can be applied. The outside temperature of the heat exchanger ranges from 150° to 190° F. The cooling water flow through the heat exchanger is regulated to maintain an exit water temperature of approximately 100° F. It is

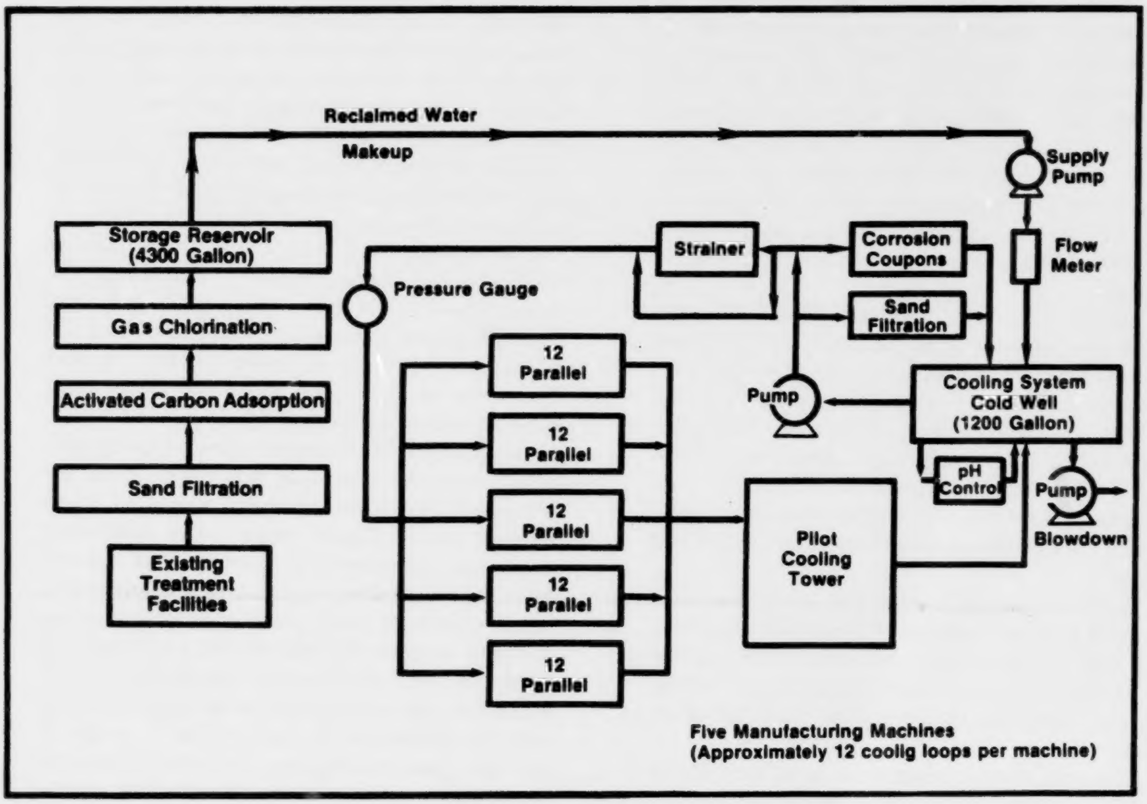

Reclaimed Water
Makeup
Supply Pump
Flow Meter
Storage Reservoir (4300 Gallon)
Gas Chlorination
Activated Carbon Adsorption
Sand Filtration
Existing Treatment Facilities
Strainer
Corrosion Coupons
Sand Filtration
Pressure Gauge
12 Parallel
12 Parallel
12 Parallel
12 Parallel
12 Parallel
Pump
Cooling System Cold Well (1200 Gallon)
pH Control
Pump
Blowdown
Pilot Cooling Tower
Five Manufacturing Machines
(Approximately 12 coolig loops per machine)

Figure 2. Schematic flow diagram — final pilot cooling system.

under this hostile environment that the cooling water and heat exchangers must function properly if the high integrity of the glass fiber is to be maintained. This meant that parameters of the reuse water for such a system had to be such that there could not be physical separation that would cause buildup on the heat exchangers which in turn would greatly affect the process—if not shut down the process completely. The hot water would then pass through cooling ponds and again no physical separation could take place. The preliminary design of the treatment included the primary and secondary systems that already existed plus sand filtration, carbon adsorption for organic removal, and finally, disinfection. To make the whole treatment workable, it was necessary to retrace some of our steps, and improve and optimize the primary and secondary phases. When this was accomplished, the primary and secondary phases were optimized in the field, based on the lab bench studies. A properly sized sand filter was designed and installed to handle 10 to 20 gallons per minute. A carbon column of like size was also installed. Of course, all of these steps were reviewed on a constant basis with the plant personnel and more particularly the production personnel. This type of coordination makes the plant a part of the whole process and the desire for a total recycle system "rubs off" on its key personnel.

The pilot system operated off the effluent from the secondary or activated sludge system. It was previously determined by the production and management personnel that the system would have to operate successfully for a period of at least 120 days. As always, there are bugs to work out in any new system. This was so at Anderson. It was necessary to operate the pilot system for 210 days instead of 120 days.

The first plateau had been reached. The pilot system proved practical and feasible—confirming our ability to construct a full-scale system to satisfy the most critical situations as well as all the variables at a complex manufacturing facility.

The next step, of course, is to collect all the data accumulated to date including parameters, preliminary design drawings, cost estimates, approvals, comments, benefits, justification, etc., and present this to management for approval of funds for construction. It usually is necessary to obtain approvals from pollution control agencies.

I found it desirable to locate a consultant at the beginning to work with the corporation personnel throughout the project as required. This keeps the consultant up to date so that when work is required, no time is lost in reviews. Owens-Corning Fiberglas had reviewed consultants and their personnel during the concept stage and selected Engineering Science, Inc., of the Atlanta office, to work with us frequently throughout the project. They performed such duties as assisting on the water balance, assisting on analysis of parameters, developing the pilot system from concept, operating the pilot system, collecting data, report writing, final design, equipment specifications, and studying and evaluating as required. All other work was accomplished by corporate staff and plant personnel.

Once all the approvals and funds were received, it was necessary to convert all the data into a final design, develop the equipment specifications, purchase materials and equipment, let contracts, and begin the construction work. This phase of the work is generally procedural; however, there are always questions, changes, and modifications to be taken care of so that the final system is workable.

The design work was completed in March 1977 and the actual fieldwork started at the same time. There were more problems than ever anticipated during this phase due to the use of newly developed materials for the first time ever in such a project. The major components were completed by September 1977. Those phases of the system were put into operation; however, recycling was never really accomplished until May 1978 and was on an intermittent basis. There were many additional problems encountered during this phase, mainly because the primary and secondary systems' efficiency was greatly deteriorated by the cold weather during the fall and winter of 1976 and 1977. At a time in the spring of 1977 when the systems should have snapped back, nothing happened. It was necessary to go all the way back to step one and concentrate on the primary and secondary phases of the operation. It took from the spring of 1977 until January 1978 to define the problems and make the corrections required. During this time many investigative techniques were performed including:

- review of chemical usage in production,
- jar testing of coagulants,
- biological treatability studies, and
- nutrient balance.

A review of production records and chemical usage indicated that not only had the cold weather affected the treatment operations, but also some changes in chemical usage in production (that were originally thought to be insignificant) had a combined effect. However, after a thorough review we still could not fully account for the poor treatment efficiencies. Therefore, jar tests were performed on the primary clarifiers to reduce colloidal emulsion carryover. Earlier studies, performed during the pilot stage of the recycle system, indicated that primary colloidal carryover would pass through further treatment, remaining in the tertiary-treated effluent. As it turned out, the jar tests were successful at developing a chemical addition scheme which could remove the suspended solids found in the raw wastewater. Once this phase of the system was properly corrected, the loading on the secondary system was reduced.

Biological treatability studies were performed next on the "improved" primary effluent. These studies indicated a nutrient deficiency existed as a result of the shift in chemical usage during production. Therefore, supplemental nutrient addition was implemented. The results were astounding—the most significant to date. With each incremental addition of nutrient, secondary effluent quality improved. In addition, analyses were performed on the secondary effluent to monitor and control the nutrient addition. These modifications enabled the primary and secondary systems to perform as they had during the original pilot design period. Efforts were made to further continue these improvements. These included modifying the sludge wastage procedure, wasting from the aeration tanks rather than the usual approach of wasting from the return sludge line. This allowed the plant operators to more easily control the sludge wastage.

The wasted sludge was piped into the aerated equalization tanks to further extract any usefulness of this biological sludge. The intent was to utilize the sludge in equalization tanks as a roughing system to reduce the impact of the raw waste on the main body of the secondary system. Our experience in defining and solving problems in this system serves as a resource upon which future projects can be approached with new insight and greater opportunity for achievement.

At this point in the presentation, it is best for me to describe our total system (See Figures 3 and 4). The industrial wastewater is collected from all of the operations at the facility in a separate sewer system. Up until the time work was started on this project, all industrial wastewater was collected in a combined sewer system with all the sanitary wastewater from the facility (which employs approximately 2,000 personnel). The industrial wastewater enters the treatment facility through a bar screen and then flows into one of the two equalization tanks. The flow to the treatment plant averages 295 gallons per minute and flow range is generally between 200 and 360 gallons per minute. The two equalization tanks are of capacities of 250,000 and 150,000 gallons, and both are equipped to provide continued aeration. The influent is collected in one equalization tank and pumped to the influent weir, which is adjusted daily, if necessary, to control the flow through the system. Excess water is collected in the second equalization tank and continually blended. I should add that there are three tanks with a total capacity of 55,000 gallons ahead of equalization that are utilized to collect shock loads. This is accomplished by cooperation and communication throughout the entire product facility. When someone has strong or other unusual wastes to discharge, a phone call is made to the treatment facility operators and the waste is tested for and, if need be, collected in one of the storage tanks. After tests are conducted, and experience plays an important role here, the waste is treated chemically and then metered into the treatment system at a predetermined slow rate to reduce the effect on the system.

Once equalization has been accomplished and the flow regulated into the system, the water enters a chemical mix tank where ferric chloride at the average rate of 10 ppm is added. Caustic soda is used to control pH, when required.

In the flocculation tank, which is next in line,

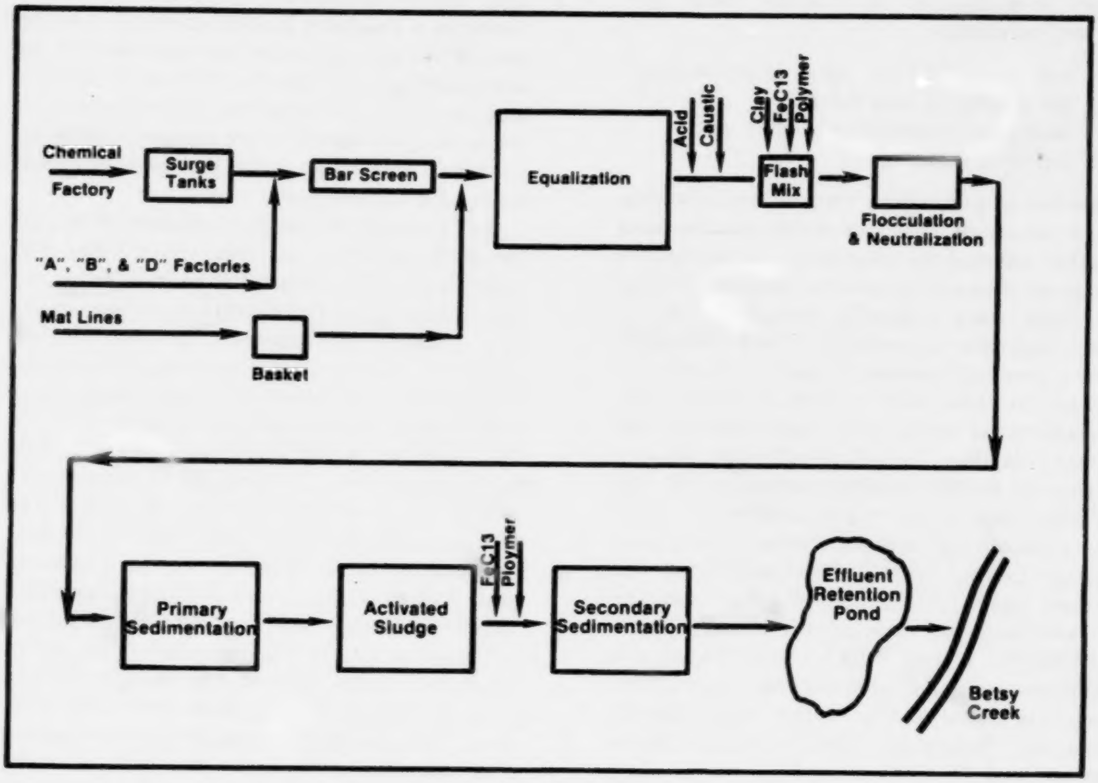

Chemical
Factory
Surge Tanks
Bar Screen
Equalization
Acid
Caustic
Clay
FeC13
Polymer
Flash Mix
Flocculation & Neutralization
"A", "B", & "D" Factories
Mat Lines
Basket
Primary Sedimentation
Activated Sludge
FeC13
Ploymer
Secondary Sedimentation
Effluent Retention Pond
Betsy Creek

Figure 3. Process flow diagram — existing wastewater treatment facilities.

an anionic polymer is added to aid flocculation, and nutrients (ammonium nitrate and phosphoric acid) are added if required. Wasted activated sludge is also added at the entry of this tank. It has been determined that the wasted activated sludge aids in coagulation and flocculation and does reduce chemical usage.

The water is mixed and then distributed to the five clarifiers. These five clarifiers were part of the original construction and were utilized as they existed, thus providing additional flexibility in the system. The total capacity of the clarifiers is 44,500 gallons providing a retention rate of 2.5 hours at average flow. The flow from the clarifiers is collected and mixed with activated sludge which is recycled at the rate of 67 percent before entering the three activated sludge tanks. Swing arm diffusers are used for aeration and approximately 1,000 ft^3/min of air is provided at average flow. The effluents from these tanks are collected and then equally distributed to the three final clarifiers. These three tanks have a total capacity of 37,400 gallons and thus provide a 2.2-hour retention time at average flow. Activated sludge is pumped off continually at a controlled flow and recycled to the head of the aeration tanks, and the wasted sludge is pumped back to the influent to the flocculation tanks. The effluent from the final clarifiers is measured in a Parshall Flume and flows by gravity to the sand filter. The sand filter design rate is 4 gpm/ft^2.

The flow is collected in a clear well and pumped into one of three carbon columns. Each of these carbon columns is 10 feet in diameter and 20 feet high with a capacity of 20,000 pounds of activated carbon. The system has the flexibility of utilizing a lead column and a lag column in series, and a third column is on standby, ready for use. There is also a fourth column in the grouping that is used for new or spent carbon storage. The entire carbon adsorption system operation is semiautomatic.

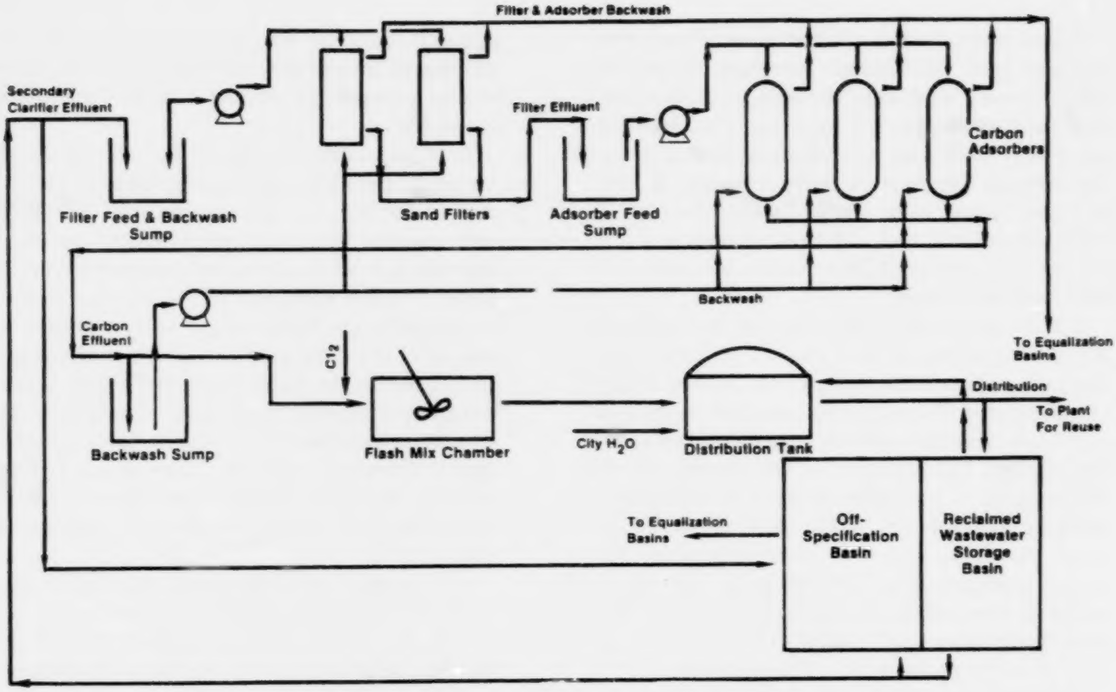

Filter & Adsorber Backwash
Secondary Clarifier Effluent
Filter Effluent
Carbon Adsorbers
Filter Feed & Backwash Sump
Sand Filters
Adsorber Feed Sump
Backwash
Carbon Effluent
To Equalization Basins
Cl_2
Distribution
To Plant For Reuse
Backwash Sump
Flash Mix Chamber
City H_2O
Distribution Tank
To Equalization Basins
Off-Specification Basin
Reclaimed Wastewater Storage Basin

Figure 4. Process flow diagram – advanced wastewater treatment facilities.

The personnel have immediate control of the system; however, valves and other operating controls operate automatically once the changes are started.

The flow from the carbon system is chlorinated and measured prior to discharge to the 230,000-gallon distribution tank. This clear well is covered to protect it from any fugitive dust and an overflow line discharges any surplus treated water to a 1,500,000-gallon holding pond. At the present time, the water in the holding pond is cycled through the sand filter and carbon adsorption system before reuse; however, a study is underway to determine if this water could be used directly as makeup into the distribution tanks. It may be necessary to cover the entire pond or a portion of it for protection.

The treated water is pumped from the distribution tank back to all phases of product operations at the Anderson plant. This is accomplished by two pumps that maintain a minimum of 44 pounds of pressure throughout the system and at a flow required by the product operations. A completely new distribution system has been installed to each area of production requiring water. The main water usage (about 60 percent) at the facility is equipment and area washdown. The remainder of the usage is in the many cooling systems throughout the plant. Cooling water is used in furnace cooling, fiber-forming heat exchangers, room and area cooling, and controlling humidity. The blowdown for the entire system is evaporation losses and wind losses throughout all of the operations. Any makeup water added at the facility over and above those few areas that require potable water is added at the distribution tank. This is done to maintain control of the water usage at the facility and continue a zero discharge system.

It may be necessary to bypass the sand filtration and/or the carbon adsorption system at times; therefore, a second pond was installed to collect this water as well as sand filter and carbon backwash water. This pond water can be pumped to the head of the system for treatment and reuse.

There have been a number of problems during the past 12 months; however, these are slowly being reduced through modifications and improvements. We have had recirculation since May 1978 with intermittent discharges to the stream. These were more frequent at first but reduced to lesser amounts until October 7, 1978, when total recirculation without any discharge was achieved. The system has operated that way ever since.

I have not made much mention of sludge in my presentation. It is a subject in itself with the new regulations being promulgated under the Resource Conservation and Recovery Act. We have been periodically making studies on the sludge, but because of the complexity of the system, it has been decided to utilize our existing system until such time as we determine that the water treatment system has been stabilized. Then we will make a comprehensive study of the total sludge problem and develop, design, and install the facilities required to properly meet all regulations.

The present sludge system includes an automatic drawoff system from each of the five clarifiers. This sludge is pumped to an aerobic digester with a capacity of 230,000 gallons. Digested sludge is drawn from the digester and deposited in a sludge lagoon. Supernatant from both the digester and the lagoon is pumped back to the equalization tanks. As mentioned previously, wasted activated sludge is also pumped to the head of the treatment system.

It is impossible to delve into all the details for such a system as is operational at the Anderson facility. To discuss any one of the specific phases is a full presentation in itself; therefore, I have attempted to review the the history of our company in the development of zero discharge. Information on the pilot work and all of the details are available in the report submitted to Mr. Max Samfield, Grants Administration Division, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, entitled "Preliminary Engineering Report – Wastewater Reuse System for Fiberglass Textile Industry," dated February 1977.

The system at Anderson is presently operating with no discharge – but one week or one month does not prove a state-of-the-art. We will not be satisfied that we have developed a zero discharge system until we get through the winter and on to next summer without upsets, but again, we have faith in the concept, the equipment, and the personnel. And, we have tasted success and are determined to make it a reality, thus meeting the 1983 standards 6 years before required to do so by law.

OPTIMIZATION OF HYPERFILTRATION SYSTEM FOR RENOVATION OF TEXTILE WASTEWATERS*

S. M. Ko and P. G. Grodzka[†]

Abstract

A computer program for design and simulation of a multistage hyperfiltration system for renovation of textile wastewater has been developed. The program is capable of practical design, parametric simulation, and cost projection of the multistage hyperfiltration system with tapered innerstages. The mathematical model is formulated based on Sourirajan's preferential sorption and solute diffusion theory. Experimental rejection and flux data of a test hyperfiltration module are required as input parameters. Empirical correlations and test results available from recent EPA-sponsored programs are utilized to calculate membrane transport parameters. Computed results for sample cases using cellulose acetate and dynamic membranes are presented. Various design and operating parameters are considered in the numerical computations to show effects of these parameters on economics of the system. This simulation program was developed in a general manner and is readily adaptable for evaluation of other reverse osmosis hyperfiltration applications.

INTRODUCTION

Hyperfiltration (also termed reverse osmosis) as a textile wastewater treatment and renovation process has been studied under EPA/IERL-RTP[‡] sponsorship to investigate the technical feasibility and the economic practicability of the separation process. A recent investigation (ref. 1) of a pilot-scale hyperfiltration facility at La France Industries, a division of Riegel Textile Corporation, successfully demonstrated the feasibility of hyperfiltration membranes for the in-plant recycle and reuse of composite textile dyeing and finishing wastewater. The applicability of the concept to a variety of composite textile wastewaters has been confirmed in a more recent study (ref. 2) at eight different textile mills encompassing eight different subcategories of the textile mills point source category (ref. 3). The scope of these studies, however, was limited to testing and evaluating a few commercial membranes using plant composite wastewater and the mixed dyehouse effluent. Furthermore, optimization of process parameters in regard to more favorable economics, e.g. energy conservation, byproduct recovery, and effluent control of the process system, were not investigated in detail.

Textile finishing wastewater contains a variety of chemicals depending upon the particular dyeing and finishing operations. The types of chemicals in the wastewater greatly affect the performance of the membranes. The effectiveness of membranes is also sensitive to the temperature of the wastewater being treated. In the interest of energy recovery, high temperature operation of the process is desirable. Thus, a parametric investigation of the separation process directed toward efficient and cost-effective design of the treatment system is required to provide the optimum performance and design information essential in the development of a full-scale system. Since experimental investigations of these parameters are not practical, such a parametric study necessitates a theoretical analysis of fundamental mechanisms involved in the hyperfiltration process and the development of a computer model of the process system. Unfortunately, however, direct extension of general reverse osmosis theory to mixed solute systems is complicated due to nonavailability of pertinent fundamental physicochemical properties of both membranes and solutes, and possible complex interactions of chemicals in such a system. Thus, the transport properties of solutes in the composite wastewater must be calculated from experimental flux and rejection data. Where such data are not available, these transport parameters may be estimated using empirical correlations (refs. 4,5).

---

*Study sponsored by the U.S. Environmental Protection Agency under EPA Contract 68-02-2614.

[†] Lockheed Missiles & Space Company, Inc., Huntsville, AL.

[‡] Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, NC.

MATHEMATICAL MODEL

The model described herein is based on Sourirajan's preferential sorption and solute diffusion theory (ref. 6), which applies simple boundary film theory (refs. 7,8) to obtain the concentration polarization of the solute (ref. 9). The effect of pressure drop due to friction losses and momentum changes on the performance of the system (refs. 10,11) is included in the model.

Membrane Model

Consider a tubular hyperfiltration module as shown in Figure 1. From the overall material balance for the differential control volume, the change in average axial velocity ($\bar{u}$) can be written as

$$-\frac{d\bar{u}}{dx} = \frac{2}{r}\, v_w \tag{1}$$

where v_w is the permeation velocity of product water (permeate) through the membrane (ft/s). Similarly, the solute material balance can be written as

$$-\frac{d(\bar{u}C_{A1})}{dx} = \frac{2}{r}\, v_w C_{A3} \tag{2}$$

where C_{A1} and C_{A3} are the molar concentrations of solute in the bulk and the product, respectively.

Now, an expression for the pressure drop in a tube in terms of friction losses and momentum changes may be obtained from an energy balance (ref. 10)

$$-\frac{dP}{dx} = CM\frac{\bar{u}^2 f}{g_c r} + \frac{\bar{u}}{g_c}\frac{d\bar{u}}{dx}$$

or substituting (1) yields (3)

$$-\frac{dP}{dx} = CM\frac{\bar{u}^2 f}{g_c r} - \frac{2\, v_w \bar{u}}{g_c r}$$

where C is the molar density of solution (lb-mole/ft^3), M is the average molecular weight of solution, f is the Fanning friction factor, and g_c is the conversion factor.

By solving equations (1), (2), and (3) simultaneously, one can compute output variables $\bar{u}$, P, and C_{A1} for the differential volume for a given set of dependent variables, product rate (v_w), and solute transport (C_{A3}). These dependent variables can be related to the feed rate ($\bar{u}$), the system operating pressure (P), and the concentration of feed stream (C_{A1}) by transport mechanisms of solute and permeate (product water) through the membrane and associated concentration polarization of solute in the high pressure side of the membrane. To obtain the expressions for v_w and C_{A3}, let us consider a differential section of the tubular hyperfiltration module shown in Figure 2. The figure

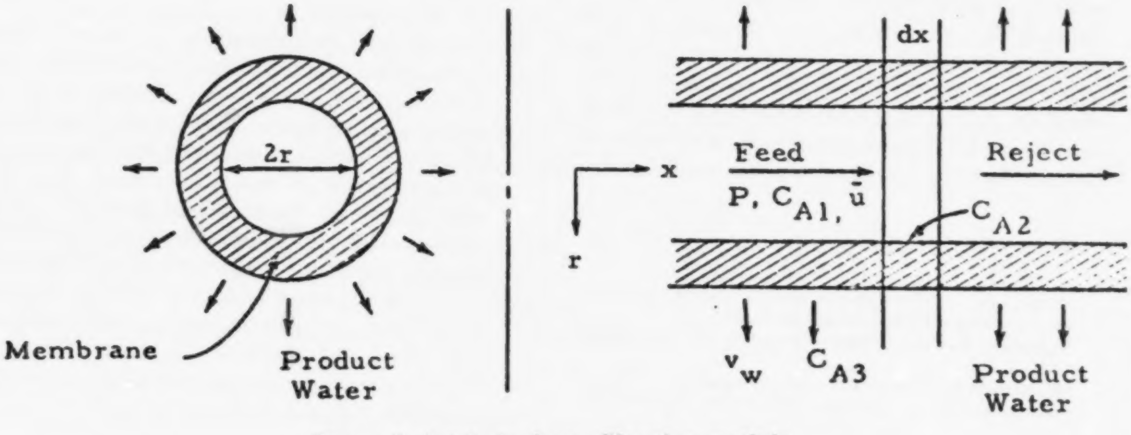


Figure 1. A tubular hyperfiltration module.

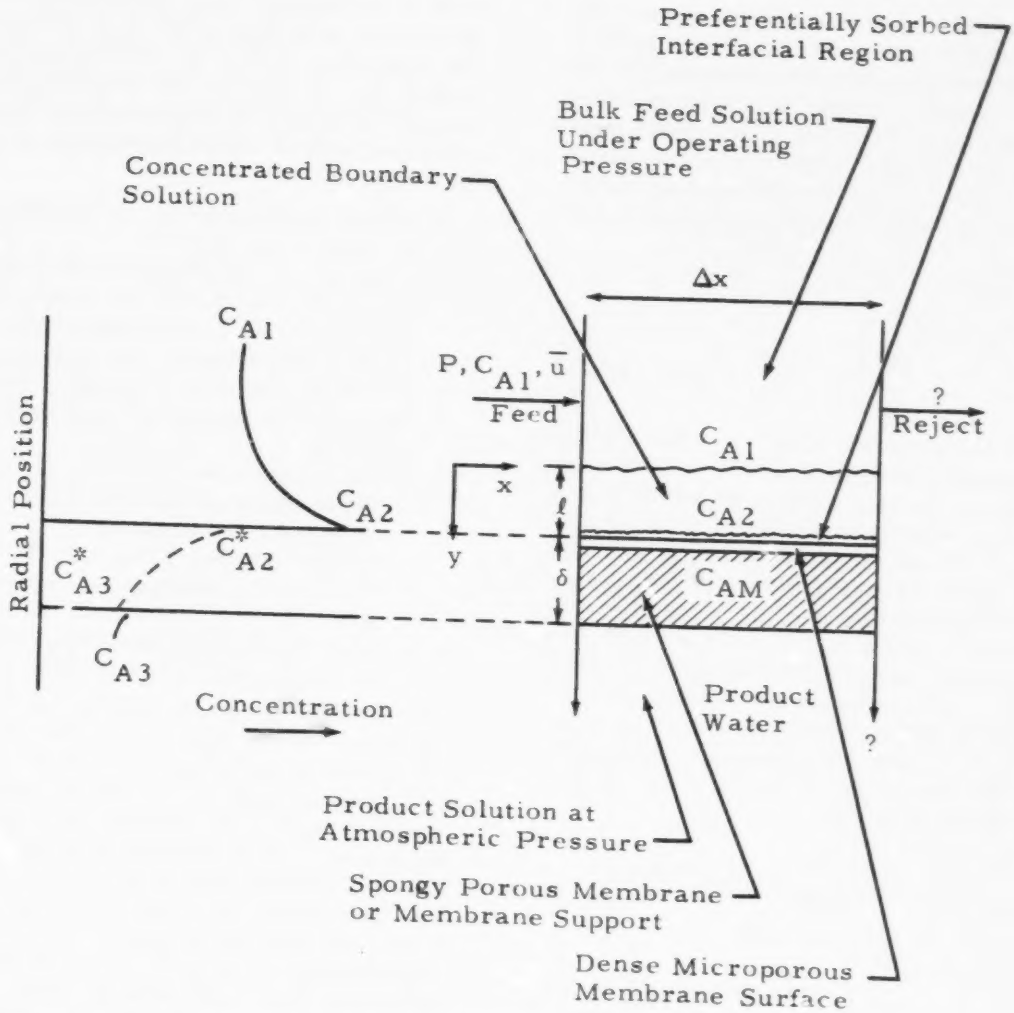

Preferentially Sorbed Interfacial Region
Bulk Feed Solution Under Operating Pressure
Concentrated Boundary Solution
Δx
C_{A1}
$P, C_{A1}, \bar{u}$
Feed
?
Reject
Radial Position
C_{A1}
x
C_{A2}
C_{A2}
ℓ
C^*_{A2}
y
C^*_{A3}
δ
C_{AM}
C_{A3}
Concentration
Product Water
?
Product Solution at Atmospheric Pressure
Spongy Porous Membrane or Membrane Support
Dense Microporous Membrane Surface

Figure 2. Concentration profile of the differential hyperfiltration module under steady state. (C^*_{A2} and C^*_{A3} denote solute concentrations in the membrane phase in equilibrium with respective concentrations in the liquid phases.)

shows a schematic of steady state concentration profile of the solute across the membrane. Due to relatively high affinity of the membrane to solvent (water) molecules, a concentration gradient is established in the interface region. Adsorbed water molecules are permeated through the microporous structure of the membrane at a rate determined by the characteristic of the membrane and the pressure exerted to overcome the osmotic pressure. Solute, on the other hand, diffuses to both directions from the interface. The preferential sorption of water molecules will develop high solute concentration right in the vicinity of the interface and thus develop a maximum concentration. This provides a driving force for the solute diffusion to both directions from the interface.

The transport of product water through the membrane (refs. 6,9) is proportional to the effective operating pressure of the system. The effective pressure is defined to be the difference between the operating pressure and the osmotic pressure exerted by the concentrated boundary layer. Assuming a linear dependency of osmotic pressure on mole fraction, we obtain the following expression. (Detailed derivation of the expression is available in reference 12.)

$$v_w = \frac{N_B}{C} \qquad (4)$$

$$= \frac{AP}{C}\left[1 - \frac{B}{PC}\left(C_{A2} - C_{A3}\right)\right]$$

N_B is the permeate water flux through the membrane (lb-mole/ft^2-s), C is the molar concentration of the bulk solution (lb-mole/ft^3), A is the pure water permeability of the membrane (lb-mole/ft^2-s-psi), P is the operating pressure (psi), and B is the proportionality constant for osmotic pressure (psi).[§]

The expression for C_{A3} can be obtained by integrating the differential equation obtained from a differential solute material balance within the concentrated boundary layer. A detailed derivation and solution of the boundary equation are presented in reference 12. The resulting expression is:

$$\frac{C_{A1}}{C_{A3}} = 1 + \frac{1}{C_{A3}B/CP + CS/AP} \qquad (5)$$

$$\exp -\left\{\frac{1}{k/S\,(C_{A3}B/CP + SC/AP)}\right\}.$$

S is the solute transport parameter[#] (ft/s) and k is the mass transfer coefficient of the solute in the solution phase (ft/s).

The set of equations (1) through (5) can be numerically solved to obtain output conditions from the differential section of the module for a given input (or initial) conditions at the inlet of the differential section. By repeating the procedure one can compute the overall performance of the module. The following input parameters are required for the performance prediction:

1. Design specifications for the system, i.e., geometry of the module;
2. Initial process conditions at the inlet of the system, that is, flow rate, feed concentrations, pressure, and temperature;
3. Physical properties of feed stream, that is, viscosity and osmotic pressure as functions of solute concentration and temperature; and
4. Transport parameters:
    a. Permeability constant (A) as a function of pressure and temperature,
    b. Solute transport parameter (S) as a function of pressure and temperature, and
    c. Mass transfer coefficient (k) as a function of dimensionless numbers.

Parameters 1 and 2 are defined by the system design specifications. The effect of these parameters on performance/cost can be investigated and an optimum set can be identified through a series of numerical computations. Parameter 3 can be obtained from the literature. In the event these data are not available from the literature, experimental measurements may become necessary. The relative magnitude of the three transport coefficients (parameter 4) will determine the shape of concentration profile and the efficiency of the hyperfiltration process. The transport coefficient can be obtained from a set of experimental measurements of the product water rate, pure water permeability of the membrane (normally given by the membrane manufacturer), and solute rejection efficiency. These parameters are temperature and pressure dependent. The dependencies can be expressed by the following equations (refs. 13,14):

$$A \;\alpha\; \exp(-\alpha P)$$

$$S \;\alpha\; P^{-\beta}\exp(-\gamma/T)\,.$$

α, β, and γ are constants, which can be calculated from experimental results. Empirical correlations published in the literature can be used to calculate the solute mass transfer coefficient (ref. 15).

[§] Note that the constant B is a very small number for organic solutes found in textile wastewaters. For such cases, the osmotic pressure term can be neglected and the flux can be written simply as: $v_w = AP/C$.

[#] S is used to denote the solute transport parameter represented by ($D_{AM}/K\delta$) by Sourirajan (ref. 6). D_{AM} is the diffusivity of solute in the membrane phase (ft^2/s). K is a characteristic constant that represents preferential sorbability of the solute on a given membrane surface. S is uniquely determined by the characteristics of specific membrane/solute combination.

Economic Model

The incremental cost for producing unit quantity of permeate water is considered to analyze the system economics. The cost elements contributing to the incremental product cost are amortized capital cost, UCC ($/kgal), and O&M costs ($/kgal). The amortized capital cost is calculated based on the installed system capital cost per unit membrane area ($/ft^2 of membrane surface). The O&M costs include membrane replacement cost, UMRC ($/kgal), pumping power cost, UPP ($/kgal), and other O&M costs, UMOMC ($/kgal). The credits to the product cost are credit from recovered water, CRW ($/kgal), and credit from recovered energy, CRE ($/kgal). The credit from recovered chemicals is not included because recovering chemicals from the concentrate usually requires additional process modifications.

The unit incremental cost for product water, UCPW ($/kgal), is written

$$\begin{aligned} \mathrm{UCPW} &= \mathrm{UCC} + \mathrm{UMRC} + \mathrm{UPP} \\ &\quad + \mathrm{UMOMC} - \mathrm{CRW} - \mathrm{CRE}. \end{aligned} \tag{6}$$

The unit costs can be obtained from vendors or actual estimations.

DESCRIPTION OF SYSTEM AND METHOD

In practical applications of the reverse osmosis process, a certain multistage design concept is desirable to achieve desired levels of product recovery and solute rejection. Three such concepts with tapered inner stages are presented in Figure 3.

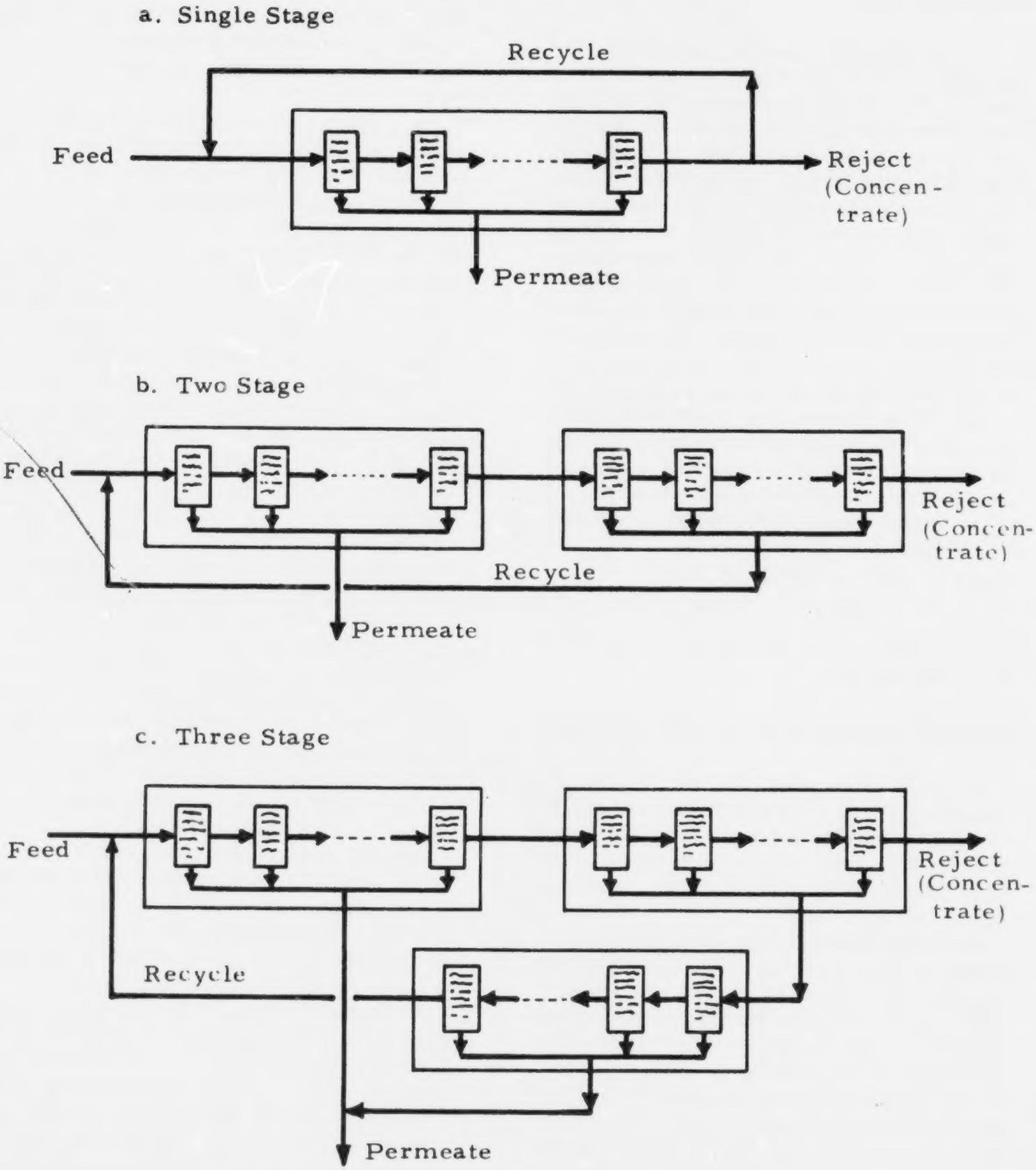
The single-stage concept employs direct recycle of a portion of the reject stream to concentrate the reject to the specified design value. In this case, the system is operated at a somewhat higher concentration than the concentration of the feed. In the 2-stage concept shown in Figure 3b, the first stage is used as a purification stage, and the second as a concentration stage. Since the permeate from the second stage has a higher concentration than the design product concentration, it is recycled to the first stage. In the 2-stage case, the concentration of the combined feed to the first stage is lower than the incoming feed concentration to the hyperfiltration system. An additional stage is employed in the 3-stage concept. The purpose of this stage is to concentrate the permeate from the second stage back to the feed concentration. This scheme provides higher system efficiency because of the reduced number of modules required for the system.

For a given design rejection and product recovery factor, the best system efficiency can be obtained when the recycle flow rate is the minimum and the concentration of the recycle stream is the same as the feed stream. Numerical results indicated that the 3-stage concept reduces the total number of modules by 30 percent and 10 percent over the single and 2-stage system, respectively. For this reason, the 3-stage concept is chosen as the system model.

The tapered innerstage design increases efficiency of the system since it reduces the concentration polarization in the boundary layer. The feed rate at the inlet of each module is maintained at the design value by reducing the number of modules within an innerstage. The number of modules for an innerstage is determined by the flow rate fed to the particular innerstage. As the bulk flow rate decreases due to permeation of water through the membrane, the level of polarization in a module increases. Minimizing the concentration polarization increases the efficiency of solute rejection efficiency as well as the product rate. The rejection increases due to reduced solute concentration in the boundary layer while higher effective operating pressure is responsible for the improvement in the product rate.

For the reasons discussed above, the tapered innerstage design is chosen for the system design purposes. Note that the innerstages are tapered with respect to the number of modules rather than the physical shape of the membrane support structure.

A schematic flow chart for the design simulation of the 3-stage tapered hyperfiltration system is shown in Figure 4. A computer program developed to solve the system of equations presented in the previous section was utilized to obtain design and economic results for the staged system. The numerical procedure for simulation of a single module employs an iterative scheme based on the Newton-Raphson method over a number of finite subsections of the module. A similar iterative pro-



a. Single Stage

b. Two Stage

c. Three Stage

Recycle
Feed
Reject
(Concentrate)
Permeate
Feed
Reject
(Concentrate)
Recycle
Permeate
Feed
Reject
(Concentrate)
Recycle
Permeate

Figure 3. Schematic diagrams of tapered multistage hyperfiltration systems.

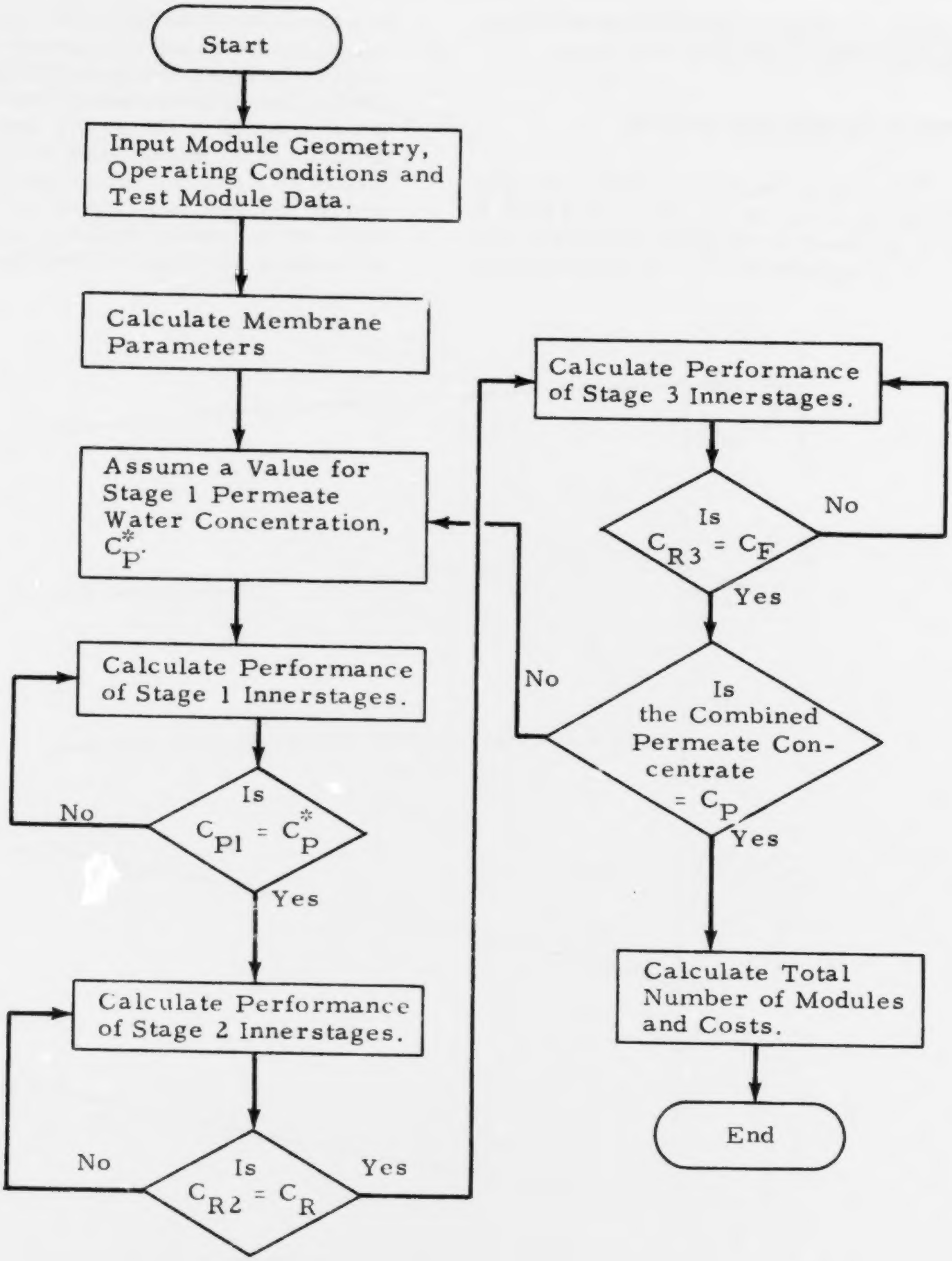

Start
Input Module Geometry, Operating Conditions and Test Module Data.
Calculate Membrane Parameters
Assume a Value for Stage 1 Permeate Water Concentration, C_P^*.
Calculate Performance of Stage 1 Innerstages.
Is $C_{P1} = C_P^*$
No
Yes
Calculate Performance of Stage 2 Innerstages.
Is $C_{R2} = C_R$
No
Yes
Calculate Performance of Stage 3 Innerstages.
Is $C_{R3} = C_F$
No
Yes
Is the Combined Permeate Concentrate $= C_P$
No
Yes
Calculate Total Number of Modules and Costs.
End

Figure 4. Flow chart of the 3-stage hyperfiltration design program. (Subscripts P, R, and F denote permeate, rejected concentrate, and feed, respectively.)

cedure is utilized to match the concentrations and flow rates to and from each stage.

RESULTS AND DISCUSSION

The numerical results of a single module performance simulation are shown in Figure 5. The case shown in the figure simulates a tubular Westinghouse module with a cellulose acetate membrane on the inside tube wall. The operating conditions and the geometry are indicated in the figure. The pressure drop for the 100-ft module is approximately 1 percent. The initial rejection is 96 percent and slightly decreases as the concentration polarization increases by 8 percent. Approximately 10 percent of the feed is recovered as permeate water and the resulting decline of the flow rate is 10 percent. The numerical results are in good

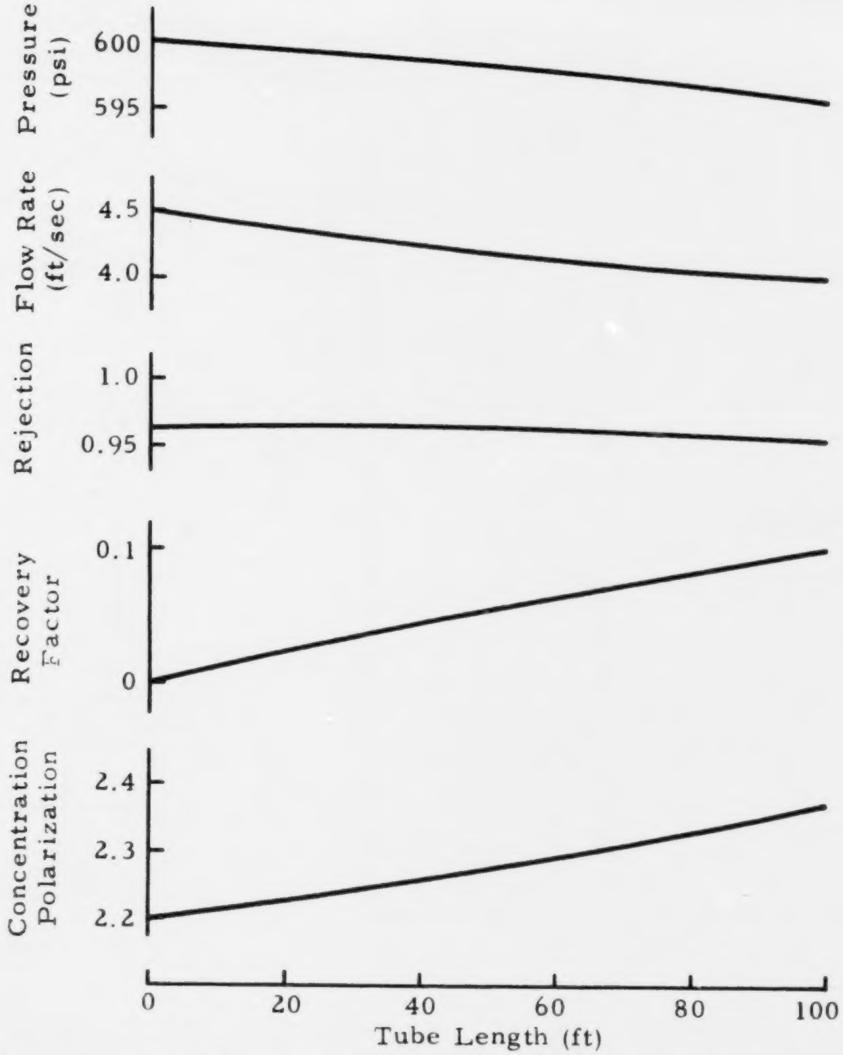


Figure 5. Performance simulation of a single tubular hyperfiltration module (feed rate = 10 gpm, temperature = 70° F, tube diameter = 1 in., cellulose acetate membrane (by Westinghouse) with flux = 4.75×10^{-5} ft/s, feed concentration = 2.0×10^{-5} lb-mole/ft^3).

agreement with the experimental results published in references 1 and 2.

From the single module simulation results, it is apparent that at least 8 stages in series are required to obtain 80 percent product water recovery if the feed concentration is low enough. For a normal textile wastewater, however, a considerably higher number of stages are required due to additional purification necessary to achieve the overall design rejection and product rate. This will be evident in the following discussions on the system design simulation of two sample cases.

Table 1 summarizes the 3-stage design simulation results for two sample 1-million-gallons-per-day (MGD) hyperfiltration systems. One is a Cellulose Acetate (CA) membrane system (Westinghouse) operating 600 psi and 70° F; the other is a Zr(IV)-PAA (polyacrylic acid) dynamic membrane system (Selas) operating at 1,000 psi and 150° F. These two membranes are selected because of readily available design and

TABLE 1. SUMMARY OF COMPUTER DESIGN SIMULATION RESULTS FOR TWO SAMPLE HYPERFILTRATION SYSTEMS OF 1 MGD CAPACITY

Item	Cellulose acetate membrane	ZR(IV)-PAA dynamic membrane
Design parameters		
Test tube rejection	0.96	0.96
Test tube flux (ft/s)	4.75×10^{-5}	11.3×10^{-5}
Permeability (lb-mole/ft^2-s-psi)	2.07×10^{-9}	2.88×10^{-9}
Solute transport parameter (ft/s)	1.23×10^{-6}	2.53×10^{-6}
Design tube diameter (in.)	1	1
Design tube length (ft)	100	100
Design product recovery factor	0.8	0.8
Design rejection	0.95	0.95
Design feed concentration (lb-mole/ft^3)	2.0×10^{-5}	2.0×10^{-5}
Design temperature (°F)	70	150
Design pressure (psi)	600	1,000
Design results		
Number of innerstages, stage 1	19	7
stage 2	11	5
stage 3	42	15
Number of modules, stage 1	846	339
stage 2	213	101
stage 3	204	99
Total number of modules	1,263	539
Total membrane area (ft^2)	31,727	13,540
Economic results*		
Total installed capital cost ($)	539,350	2,301,700
Capital amortization cost (cents/kgal)	24	102
Membrane replacement cost (cents/kgal)	79	2
Pumping power cost (cents/kgal)	15	25
Other O&M costs (cents/kgal)	10	20
Credit for recovered water (cents/kgal)	40	40
Credit for recovered energy (cents/kgal)	0	67
Total unit cost (cents/kgal)	88	42

*The unit cost basis is obtained from a recent study estimation (ref. 2). More detailed cost breakdown is described in the reference.

cost information (refs. 1,2). The transport parameters are calculated from experimentally measured rejection and flux data from the references. The two systems are designed for a product recovery factor and rejection of 0.8 and 0.95, respectively. The unit cost information was obtained from vendors and recent study estimations (refs. 1,2).

The computed total numbers of modules 1 in. in diameter and 100 ft long for the CA and dynamic membranes are 1,263 and 539, respectively. The corresponding membrane areas required are 31,727 and 13,540 ft^2. The higher surface area requirement for the CA membrane system is due to the smaller permeability of water through the membrane. The unit

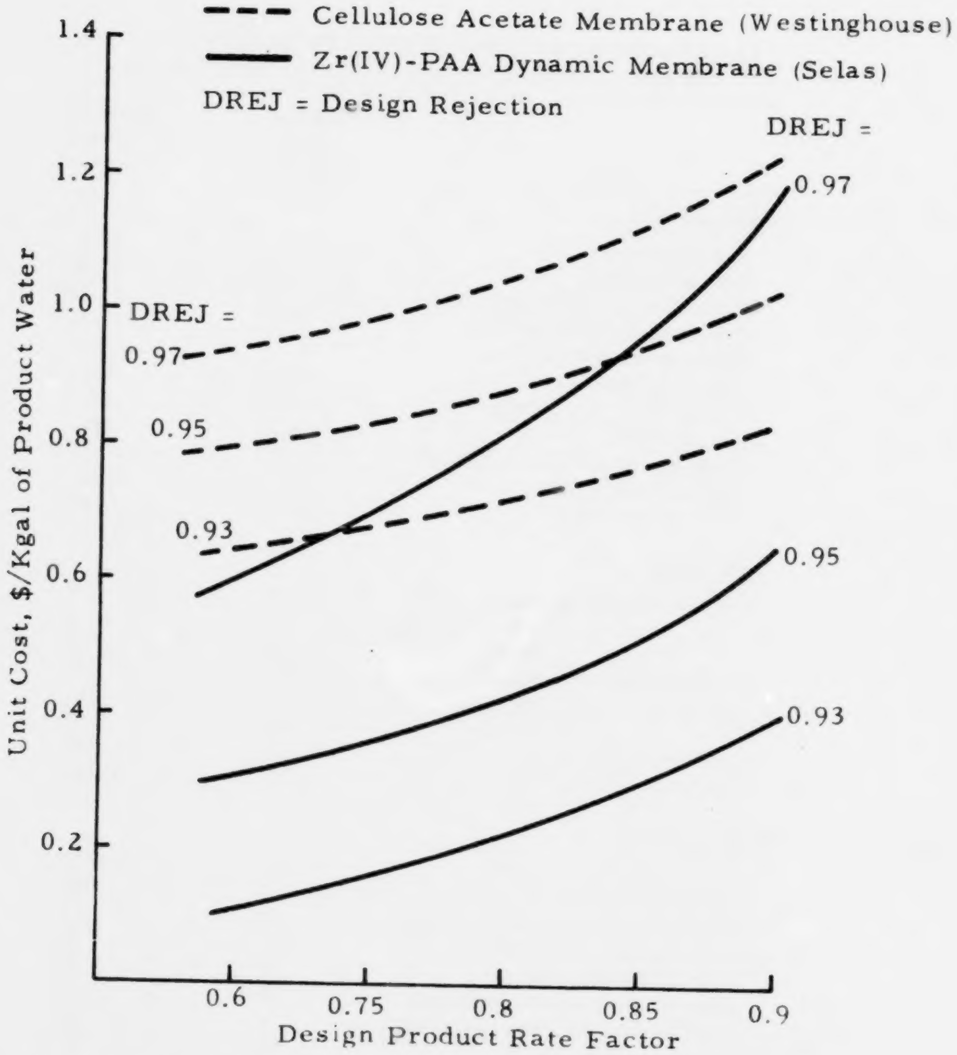


Figure 6. Effect of design product rate factor and rejection on unit cost (feed rate = 10 gpm, tube diameter = 1 in., temperature = 70° F for CA membrane and 150° F for dynamic membrane, pressure = 600 psi for CA membrane and 1,000 psi for dynamic membrane).

cost for producing 1,000 gallons of permeate water is 88 cents for the CA system and 42 cents for the dynamic membrane system. It is noted that the major cost element for the CA system is the membrane replacement cost, while the capital amortization cost makes the largest cost contribution, and the credit from recovered energy is significant enough to cause the dynamic membrane to be attractive. It should be noted that the design and operation conditions used are for illustration purposes and do not represent a typical case.

To demonstrate the range of applicability of the developed model and to investigate the effects of various design parameters on the economics of the system, a series of parametric studies is performed. The results are shown in Figures 6 and 7.

Figure 6 shows the effects of design product rate factor and solute rejection on the unit cost. The effect of design product rate factor on the unit cost is relatively moderate. The design

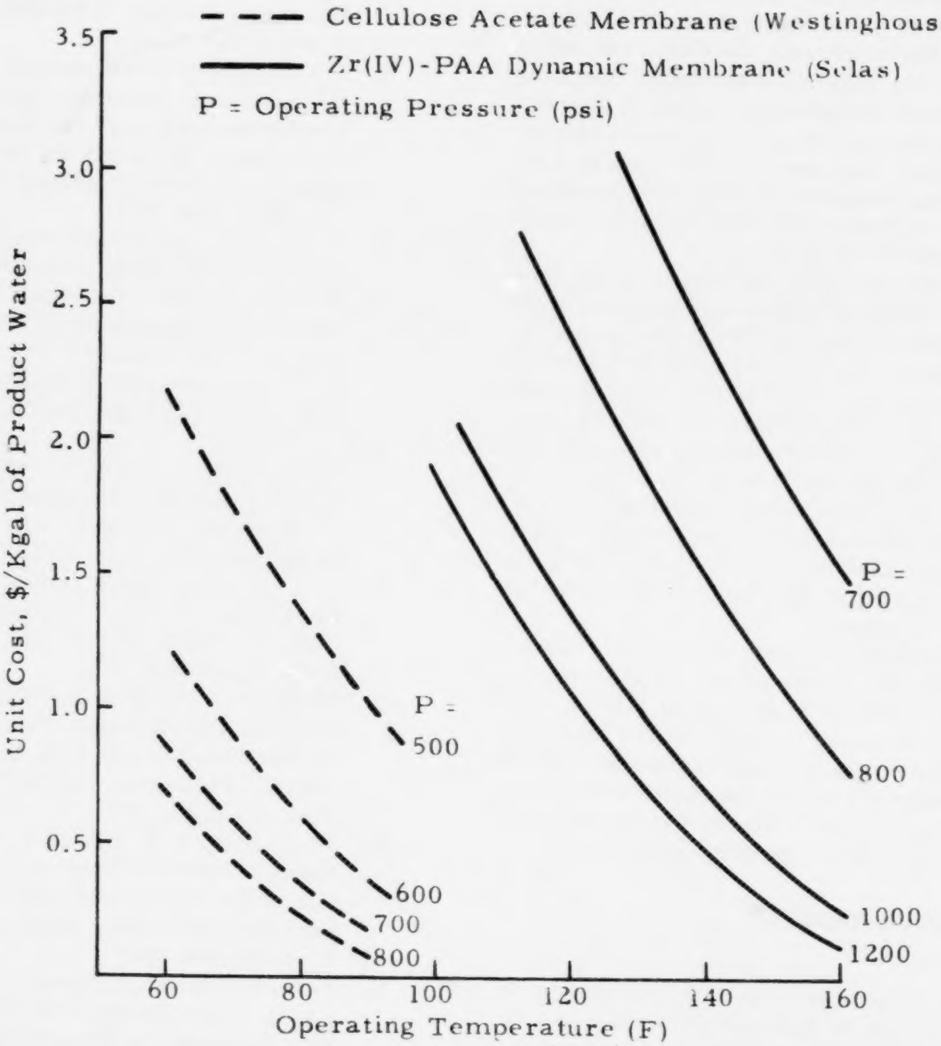


Figure 7. Effect of operating temperature and pressure on unit cost (feed rate = 10 gpm, tube diameter = 1 in., design rejection = 0.95, design product rate factor = 0.8).

rejection factor has a more pronounced effect on the cost of the dynamic membrane system. Significantly lower unit cost can be obtained at slightly lower design rejection for the dynamic membrane. On the other hand, the effect of design rejection is less significant in the CA membrane. Thus, a proper combination of these two membrane systems may be desirable when a higher design rejection is necessary due to more stringent quality requirements for reuse of the permeate water.

Figure 7 shows the effects of operating temperature on the unit cost with operating pressure as a parameter. Due to characteristics of the membranes, the effects are shown only for the respective applicable operating temperature and pressure ranges. It is shown that the unit cost is generally lower at higher temperature and pressure and a strong function of temperature and pressure as compared to those of product recovery factor and rejection shown in Figure 6.

The unit cost does not include credit from possible reuse of the chemicals contained in the concentrated reject stream. A net saving can be realized if the chemical credit is included in the computation of the unit cost. Although high temperature and pressure operation is desirable in the interest of achieving lower unit cost or even net savings, it is limited by excessive maintenance costs at high operating temperature and pressure. It is noted that the maintenance cost used in the computations does not reflect this effect but rather a flat estimated average is assumed.

In summary, the model developed is capable of predicting system performance as well as analyzing system economics to find an optimum set of design parameters. The reliability of computer results is largely dependent on the availability of rigorous cost information on the system as well as the accuracy of the test module data/membrane specifications.

ACKNOWLEDGMENT

The authors are especially grateful to Dr. J. L. Gaddis of Clemson University and Dr. C. A. Brandon of Carre, Inc. for their contributions to this study and for their comments on the mathematical model. The EPA project officer for this project was Dr. Max Samfield of IERL/RTP and his support and interest in this study are also gratefully acknowledged.

REFERENCES

1. C. A. Brandon and J. J. Porter, "Hyperfiltration for Renovation of Textile Finishing Plant Wastewater," EPA-600/2-76-060, March 1976.
2. C. A. Brandon, J. J. Porter, and D. K. Todd, "Hyperfiltration for Renovation of Composite Wastewater at Eight Textile Finishing Plants," EPA-600/2-78-047, March 1978.
3. U.S. Environmental Protection Agency, "Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Textile Mills Point Source Category," EPA-440/1-74-022-a, June 1974.
4. A. Shindler, unpublished results developed under EPA/RTP sponsorship.
5. H. G. Spencer and J. L. Gaddis, "Hyperfiltration of Nonelectrolytes: Dependence of Rejection on Solubility Parameters," paper presented at EPA Symposium on Textile Industry Technology, December 5-8, 1978.
6. S. Sourirajan, *Reverse Osmosis*, Academic Press, New York, pp. 176-184, 1970.
7. S. Sourirajan, *Reverse Osmosis*, Academic Press, New York, pp. 185-188, 1970.
8. P. L. T. Brian, "Mass Transport in Reverse Osmosis," *Desalination by Reverse Osmosis*, Ulrich Merten, ed., The MIT Press, Cambridge, 1971.
9. W. Pusch, "Concentration Polarization in Hyperfiltration Systems," *Reverse Osmosis Membrane Research*, H. K. Lonsdale and H. E. Podall, eds., Plenum Press, New York, pp. 43-57, 1972.
10. W. L. Griffith, R. M. Keller, and K. A. Kraus, "Parametric Study of Hyperfiltration in Tubular Systems with High Permeability Membranes," *Desalination*, Vol. 4, pp. 203-308, 1968.
11. J. S. Johnson, Jr., L. Dresner, and K. A. Kraus, "Hyperfiltration (Reverse Osmosis), *Principles of Desalination*, K. S. Spiegler, ed., Academic Press, New York, pp. 345-439, 1966.

12. S. M. Ko and P. G. Grodzka, "Study of Hyperfiltration Processes for Treatment and Renovation of Textile Wastewater," to be published.
13. S. Sourirajan, *Reverse Osmosis*, Academic Press, New York, pp. 191-202, 1970.
14. J. L. Gaddis, private communication dated May 24, 1978.
15. S. T. Hwang, and K. Kammermeyer, *Membranes in Separations*, Wiley-Interscience, New York, pp. 351-359, 1975.

NOTE: After the paper was given at the conference, objections were raised stating that the costs given for the cellulose acetate membrane were too low. EPA, through its contractor, solicited cost information from three cellulose acetate membrane manufacturers. The manufacturers refused to supply such information, and, therefore, the contractor used the only information available as indicated in the cited reference.

EPA would welcome additional cost information, which should be sent directly to the Project Officer.

In reviewing this and the other papers on hyperfiltration presented at the conference readers should be aware that, in the projects discussed, one is dealing with dilute solutions of largely nonelectrolytes which have low osmotic pressures.

SOLVENT RECOVERY FROM TEXTILE DRYERS

Nathan R. Shaw*

Abstract

Solvents are used throughout industry as vehicles to carry coatings onto various products, diluents, cleaners, and intermediates in the production of other products. In these capacities, hydrocarbon solvents are used in virtually all industries. The textile industry is no exception. This paper will explore some solvent uses.

Two frequently encountered uses of solvents in the textile field have to do with the application of coatings and, of course, in scouring and/or cleaning of fabrics prior to dying or other finishing operations. In both cases, the final step is to remove the solvent that has remained in the fabric by drying.

The most frequently utilized solvents for these applications are trichloroethane, trichloroethylene, or perchloroethylene. Economic considerations make it desirable to recover and reuse these solvents. Existing and/or pending EPA regulations often make their recovery mandatory. Fortunately, vapor-phase carbon adsorption technology, which satisfies both existing and pending EPA regulations, is readily available for recovery of these materials so solvents may be reused.

Most of us, by this time, are familiar with the basic technology of vapor-phase carbon adsorption. For those of you not familiar with the basic equipment of the process and as a refresher for the rest, the basic equipment configuration consists of a blower and motor assembly to move the solvent-laden air through the activated carbon bed, one or more vessels containing activated carbon, a steam distribution system used for regeneration of the carbon beds, a condenser to convert the solvent/steam vapor to a liquid, and a decanter for separation of the organic and aqueous phases.

During adsorption, solvent-laden air from the process enters the system through the blower and passes through the bed of activated carbon where the organic material is adsorbed. The clean air passes out the exhaust valve to atmosphere.

When the carbon is saturated with the organic component, the bed is isolated from the process and regenerated with low pressure steam. During this period, the second bed is placed on adsorption giving a continuous operating cycle.

During desorption, low pressure steam flows in a direction countercurrent to that direction utilized during adsorption. The thermal energy provided by the steam heats the carbon, revolatilizes the organic material, and then acts as a carrier gas to move the organic vapor into the condenser section where it is reduced to a liquid. It then flows by gravity to the decanter where, if the water is immiscible and is of a different density than the condensed steam, it will separate forming an aqueous and organic layer that can be removed from the decanter by gravity flow.

Solvent recovery systems for coating and scouring applications are usually small, skid-mounted units. One such system consists of two 36-in. diameter adsorption vessels and related equipment, as already discussed. This system is processing 700 SCFM of solvent-laden air containing 24.9 kg (55 lb) per hour of 1,1,1 trichloroethane. The solvent is used as a vehicle in the application of an antishrink chemical to a web of fabric. It literally locks the fibers together to prevent shrinkage. This process operates 24 hours per day, 6 days per week. Solvent-laden air is picked up from the entering and existing ports of the dryer.

Utilities required for operation of the system are as follows:

- Electrical (3 hp) = 2.24 kWh
- Steam = 123 lb/h at 15 psig
- Water = 14 gal/min
- Compressed air = negligible.

---

*Eastern Sales Manager, VIC Manufacturing Company, Minneapolis, MN.

Preceding page blank

Operating costs for the system can be calculated to be less than $1,600 per year per 8-h shift using the following cost factors:

- Electrical power at $0.035/kWh
- Low pressure steam at $3.25 per 453.6 kg (1,000 lb)
- Water at $0.20 per 3,785.4 liters (1,000 gal).

Value of recovered solvent at $0.21 per pound is $92.40 per 8-h shift, or $27,700 per year per shift. In other words, after subtracting operating costs, the solvent recovery system generates over $26,000 per year of reusable solvent. Total system cost was less than this amount as originally purchased. Installation costs are easily recovered by the second-shift operation, and the third shift is profit. This system was fully amortized in 1 year.

Another solvent recovery system involves the recovery of perchloroethylene from a wool scouring operation. Three thousand SCFM of solvent-laden air contaminated at a rate of 45.4 kg (100 lb) per hour is being processed. Solvent-laden air is from a bank of dryers and from the deodorizing exhaust of two automatic scouring machines. At a value of $0.20 per pound, this system generates $40,000 per year of reusable solvent. Regeneration of the beds occurs once every 3 hours.

Utilities required for this system are:

- Electrical (20 hp) = 15 kWh
- Steam = 238.1 kg (525 lb) per hour
- Water = 219.6 liters (58 gal) per minute
- Compressed air = negligible.

Using the same cost figures as in the previous example, and remembering that the utilities are used only approximately one-third of the time, operating cost is calculated at approximately $3,000 per year. The value of recovered solvent is more than $37,000 per year after subtracting operating costs. The initial cost of recovery equipment was less than $20,000. Installation was less than $10,000. This system was fully amortized in less than 1 year.

The expected life of the systems described above is 7 to 10 years or longer with proper maintenance. A most important additional benefit is compliance with EPA regulations.

The examples used above describe textile dryer applications well suited to vapor-phase adsorption techniques. There certainly are many more applications involving various solvents which, if even with longer amortization times, still offer a viable solution to energy conservation and compliance with environmental regulations.

SOLVENT DYEING OF NYLON CARPET USING THE STX SOLVENT DYEING PROCESS

Charles C. Wommack*, M. Pierre Favier†

Abstract

Clean technologies result from an efficient process and the complete recycling of effluents. The STX solvent dyeing process has been developed up to the pilot stage in the field of nylon carpet piece dyeing. It utilizes, in place of water, two solvent fluids—perchloroethylene and methanol—which, although perfectly miscible in each other, have different characteristics. The French Textile Institute has shown that a mixture of these two solvents penetrates into the nylon fiber in a manner far superior to the penetrating effect of water or of either of the two solvents used separately. This effect is maximized when the methanol is removed by distillation. Good penetration of the fiber is required for best dye fastness, maximum dye exhaustion, and minimum energy consumption.

Rhone-Poulenc has developed the equipment and has selected commercially available dyes that are soluble in methanol and insoluble in perchloroethylene. The dye exhaustion is complete and no added chemicals are needed. Besides the carpet and the dyes, the only products used are the two solvents, which are recycled through a recovery system that removes the maximum amount of residues from the carpet and the air. No process water is used in contact with either the fiber or the dyes in the STX solvent dyeing process. Rhone-Poulenc hopes to support efforts by an American company to conduct a demonstration program that will provide a measurement of the benefits to the carpet industry in terms of product quality, supply and discharge of water, and reduction of the energy requirements. An additional objective of the envisioned demonstration program is to document the economic factors involved in the full commercialization of the process.

INTRODUCTION

Rhone-Poulenc Industries is a large-scale chemical manufacturing firm located in France. As a result of its research in the area of dye processes, a new and entirely clean technology has been developed regarding the pilot-plant stage in Europe. It is recognized that the carpet industry of the United States, due to its concentration in small geographic areas and its much greater reliance on the use of nylon fiber in comparison to carpet manufacturers in Europe, would be able to realize the benefits offered by the new dye process much more rapidly than would be possible in Europe. Based on these considerations, the STX solvent dyeing process is being offered to American carpet firms interested in seeking to achieve full commercialization of the process.

Direct energy requirements of the U.S. textile industry during 1971 (the most recent year for which comprehensive data are available) were equal to approximately 67 million barrels of oil. About 60 percent of the total energy presently used by the textile industry is consumed in wet processing. Approximately 125 billion gallons of water are consumed annually in this processing. Much of this water, when discharged, includes appreciable quantites of both organic and inorganic chemicals which require extensive and expensive waste treatment. The required treatment processes also consume large volumes of energy. Thus, high energy consumption associated with the dyeing process and with the treatment of waste discharges are two primary concerns of the textile industry.

The STX process was developed in France as a joint venture of some of France's largest industrial concerns and the government of France. The STX solvent dyeing process, if shown to be economically and technically feasible on a large volume basis, could have significant potential benefits that go well beyond the immediate needs and concerns of any single company. It is estimated that energy savings through use of the STX process

---

*Wommack and Company, Atlanta, GA.
†Rhone-Poulenc-Chimie Fine, Paris, France.

will be on the magnitude of 60 to 70 percent when compared to present methods of dyeing. Additionally, since the process eliminates the need for process water, there are no effluent discharges. Consequently, implementation could result in significant industry-wide environmental benefits as well as significant savings in the energy required for industrial processing and treatment.

The objective of a full-scale demonstration project would be to conclusively demonstrate that the solvent dyeing process can result in significant environmental benefits and production cost savings (primarily through reduced energy consumption), and also result in a higher quality product or at least a product comparable in quality to that produced with conventional dyeing processes. The development of an effluent-free technology is a difficult and long-range venture. When success comes, the reward is a substantial savings of energy and materials. These savings stem from the fact that the first step in the new development is a careful analysis of the conditions to do a good job. It was an analysis of this type in the field of textile dyeing which lead to the STX dyeing systems.

CONDITIONS NEEDED TO PRODUCE QUALITY TEXTILE DYEING

The process of imparting color to textiles in all cases requires that the fibers of the textile be brought into contact with a dye chemical. To achieve good color fastness, the dye chemical must penetrate deeply into the fiber or must chemically react with the fiber, or both. Uniformity or evenness of coloration requires that each fiber of the textile be afforded equal opportunity to contact the dye chemical. This uniformity is normally achieved either by agitating or moving the textile, by pumping the dye chemical through the textile, or both.

All dyeing machines are designed to produce these conditions so that good quality results in terms of color fastness and uniformity of coloration. Figure 1 represents the typical dyeing machine and its various functions. In this diagram, the dye chemical is a liquid in which the textile is immersed. Penetration of the fiber is enhanced by using the heater to raise the temperature of the liquid and the textile. Uniformity of coloration is achieved by pumping the liquid.

In current practice, such a dyeing machine would use water as the liquid for carrying the dye chemical. Not only is water very inexpensive, but its characteristics are familiar to everyone and it performs the following functions needed for dyeing fairly well.

- It acts as a wetting and penetrating agent.
- It carries the dye chemicals and spreads them evenly.
- It is a good heat transfer agent for heating the fiber and equalizing temperature.
- It ionizes chemicals.

There are, however, many compromises which must be made chemically when using water to constitute the dyebath liquid. These compromises result in less than total transfer of dye chemicals from the dyebath to the textile fibers. Even when an assortment of other chemicals is used to promote the transfer of dye from the dyebath to the fiber, a portion of the dye chemicals remains in the water. Due to these factors, dyeing systems which use water as the carrier of the dye chemicals have the following inherent characteristics:

- All of the dyes are not used to dye the fiber.
- Some of the dyes remain in the bath, which must be reclaimed.
- Some of the dyes are left on the surface of the fiber when the water is removed. This residue makes it necessary to rinse the textile material, thus polluting the water used for rinsing.
- The chemicals used to improve dye quality are themselves a cause of pollution.

THE STX SOLVENT DYEING PROCESS

In the STX solvent dyeing process, no water is used in contact with the textile fibers or the dye chemicals. Instead of water, a mixture of two liquids is used to carry the dye chemicals. In the dyeing of nylon, the two liquids found to perform best are perchloroethylene and methanol. During the dye cycle in the STX process, one of the two components of the dyebath is progressively removed. Since the dye chemicals chosen are soluble in only the component of the dyebath that is removed, complete trans-

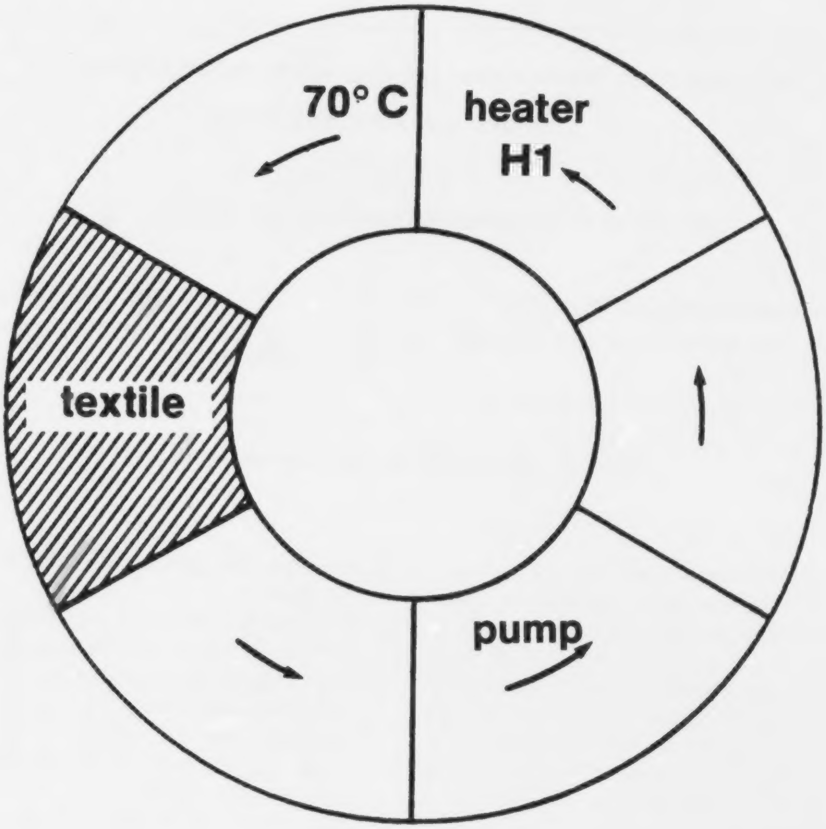


Figure 1. Basic dyeing principle.

fer from the dyebath to the fiber is assured (see Figure 2).

In the case of nylon dyeing, the dye chemicals chosen are soluble in methanol and insoluble in perchloroethylene. During the dye cycle, the methanol is removed by distillation.

The diagram shown in Figure 3 represents the dyeing machine used in the STX solvent dyeing pilot plant in Europe. As can be readily seen, the principles involved are very similar to those shown in Figure 1. The only difference is the addition of a system for diverting a portion of the liquid through a second heater, which brings the temperature to a level high enough to produce rapid distillation of methanol. It should be noted that even this distillation temperature is comparable to or lower than the normal operating temperatures of most conventional dyeing machines. In the pilot plant, the maximum temperature reached in the main circuit was 70°C (158°F) and in the secondary circuit the temperature was brought to 93°C (200°F). Since the mixture of perchloroethylene and methanol starts to boil at 65°C (149°F), it is evident that rapid and complete distillation of methanol is achieved at the temperature used.

FACTORS IN THE SELECTION OF SOLVENTS

Before going into more detail about the dyeing cycle and the pollution problems encountered, an explanation of some of the guidelines to the selection of the solvents for the STX process is in order. The solvent mixture must

A CHANGE OF COMPOSITION OF THE DYEBATH WILL MOVE
THE DYE TOWARDS THE FIBER

THIS CHANGE OF COMPOSITION WILL BE MADE :

IN CONVENTIONAL SYSTEMS	IN THE STX SYSTEM
BY ADDING CHEMICALS TO THE WATER	BY EXTRACTION OF ONE OF THE SOLVENTS

Figure 2. Change of dyebath composition.

allow a good dissolution of the dyes and a good penetration of the dyes into the fibers. The dyes must then stay in the fibers. The only industrial machines built to date have used the two solvents, perchloroethylene and methanol, in the ratio of 90 parts of perchloroethylene to 10 parts of methanol. Other solvent combinations have been used in the laboratory and may prove to be better for fibers other than nylon. For nylon dyeing, the perchloroethylene and methanol combination was found to perform best. Perchloroethylene is a widely used product in the dry cleaning industry. Its boiling point is fairly high 121° C (250° F), giving ample freedom in the selection of the best dyeing temperature. Methanol is also a readily available material, and its boiling point of 64° C (148° F) is high enough to enable operation above the fibers' transition point, yet low enough to permit easy distillation.

As previously mentioned, the dyestuffs used are soluble in methanol and insoluble in the perchloroethylene. The result is that the mixture of perchloroethylene-alcohol-dye penetrates the fiber, the distillation of the alcohol deposits the dye into the fiber (this dissolution is probably induced by the presence of free NH_2 radicals), and exceptionally high quality dyeing is achieved.

The work done by the French Textile Institute following the development of the STX process has determined that the role played by methanol in the process is as a carrier enabling effective dye penetration to the very heart of the fibers.

Water will not swell polyamide until temperatures are above the transition (around 49°C [120°]). Methanol, even below 21°C (70°F), will wet the surface of the fiber and will quickly penetrate to the center of the fiber even though it is unable to open the finer pores.

Because of these factors, methanol is not retained in the macromolecular material. This result is shown by the reversible stretch under tension of nylon fibers when they are immersed into methanol (see Figure 4). The tension is low and does not affect the crimp.

Perchloroethylene has a swelling effect much lower than the swelling effect of water. However, when perchloroethylene is mixed with methanol, there is a carrying effect. The mixture penetrates the fibers well below 60°C (140°F). The amount of perchloroethylene absorbed depends on the amount of methanol in the mixture as shown in Figure 5. A study of the perchloroethylene content within a section of fiber, which has been immersed for 1 hour at 21°C (70°F) in a mixture of 90 percent perchloroethylene to 10 percent methanol, confirms the carrying effect of the methanol.

The penetration of the chlorinated solvent is again shown in Figure 6. The fibers have been impregnated for 1 hour at 21°C (70°F) by the mixture of solvents. They have then been dryed at 38°C (100°F) for 24 hours, then at 175°F for 2 hours. The curves show the pene-

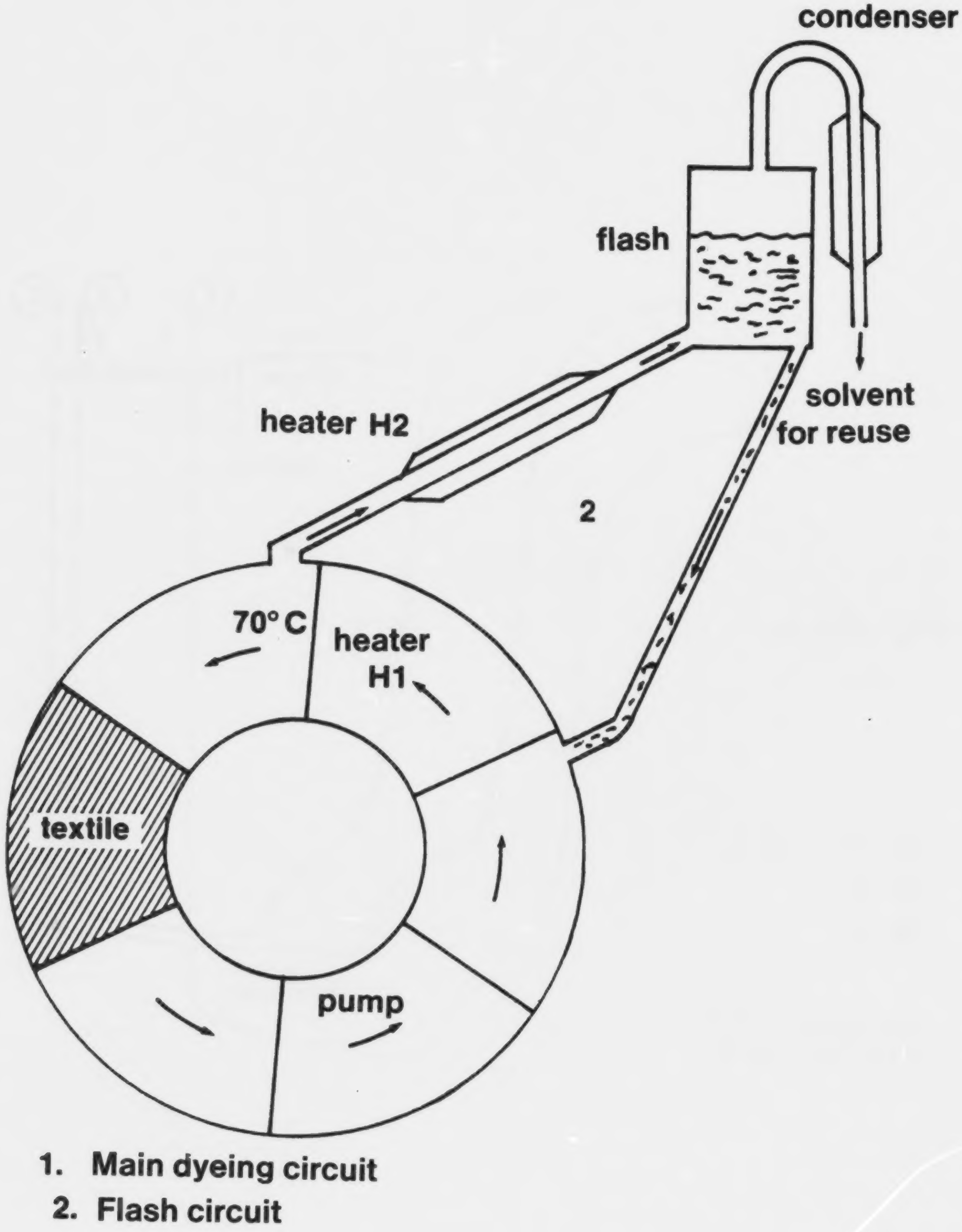

condenser
flash
solvent for reuse
heater H2
2
70° C
heater H1
textile
pump
1. Main dyeing circuit
2. Flash circuit

Figure 3. Principle of flash (liquid phase PER + methanol).

FIGURE 4

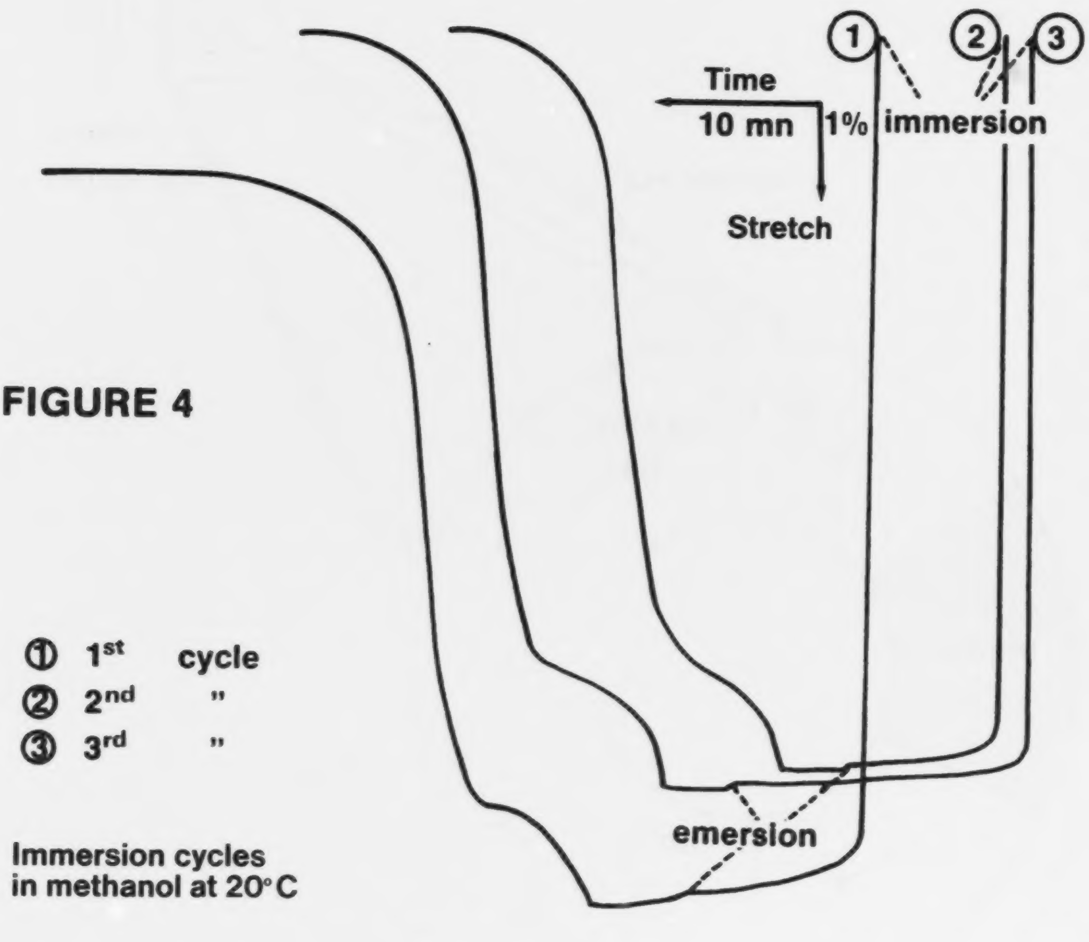


Figure 4. Immersion cycles in methanol at 20° C.

CONCENTRATION OF METHANOL (%) / TEMPERATURE (°C)	0	5	10	20	30
50	0, 00	0, 02	0, 08	0, 20	0, 15
70		0, 08	0, 17	0, 40	0, 20
80		0, 09	0, 29	0, 47	0, 39

Figure 5. Quantity of perchloroethylene adsorbed by polyamide 6-6 in relation with temperature and concentration of methanol ($cm^3 . G^{-1}$).

tration at different temperatures. It is especially high when perchloroethylene is replaced by trichloroethane, yet is much more volatile.

Because of this penetration, it is necessary, industrially, to use a steam stripping of the fibers in order to completely remove the chlorinated solvents from the fiber.

POLLUTION CONTROL

In the previous sections, we have described a dyeing process in which:

- No chemicals are added to the dyebath.
- The dyes are entirely exhausted from the dyebath.
- The dyes penetrate exceptionally deep into the fiber.

We will now look at each phase of the dyeing and drying cycle and discuss pollution hazards involved in the STX solvent dyeing process.

Figure 3

The dyebath is a mixture of perchloroethylene and methanol. The dyeing cycle has a duration of 1.30 hours. During this time, the only opening of the system to the outside atmosphere is through the methanol condenser. The temperature in this location is kept well below the boiling point of the dyebath (65° C [149° F]).

We can thus consider the dyeing circuit as a closed system. It should be noted that other efforts made towards dyebath reuse with aqueous systems use batch-type closed circuits and require fairly sophisticated pieces of equipment.

At the end of the dyeing cycle, all of the methanol has been extracted through the condenser. It can be reused for another cycle, even with a different shade. The only liquid left in the machine is perchloroethylene. This solvent will have dissolved the spinning oils and other greases contained in the carpet. Only a fraction of this oil will be deposited back on the carpet during the drying cycle. Our experience in the pilot plant is that it is adequate to recycle 10 percent of the perchloroethylene used in the machine, for each cycle, thus obtaining a perfectly clean carpet.

Figure 7

At the end of the dyeing cycle, the perchloroethylene is dumped into a storage tank. Except for the 10 percent which will be recycled, it will be immediately available for use in the next dyeing cycle. The carpet, still in the machine, is soaked with perchloroethylene. The solvent will be mechanically extracted by forcing air through the carpet at 71° C (160° F). This could be done continuously while the carpet is being unrolled. In order to avoid air contamination, the machine is equipped with a closed drying circuit, quite similar to the dyeing circuit. The drying cycle lasts 2 hours; the

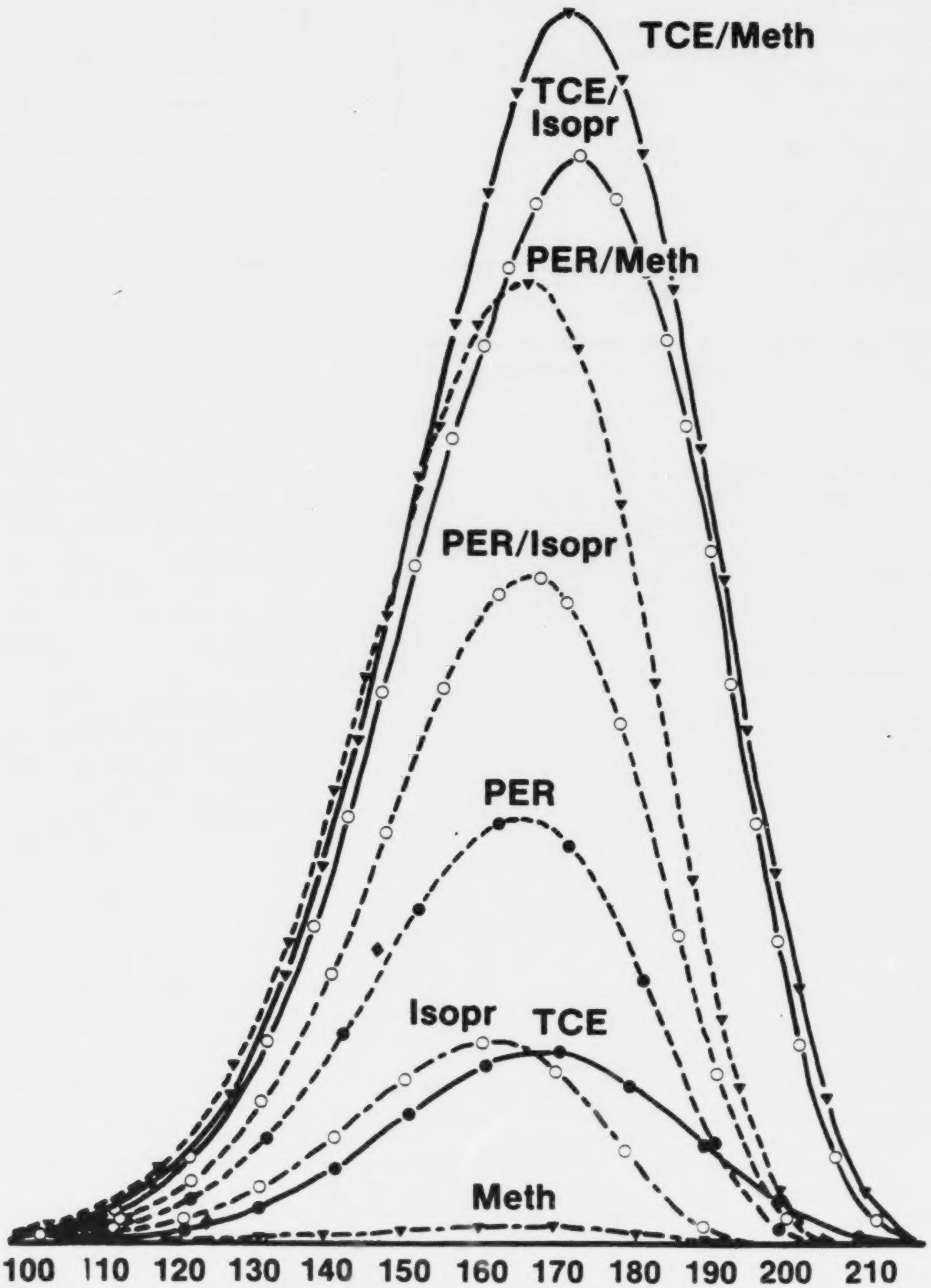


Figure 6. Penetration of chlorinated solvent.

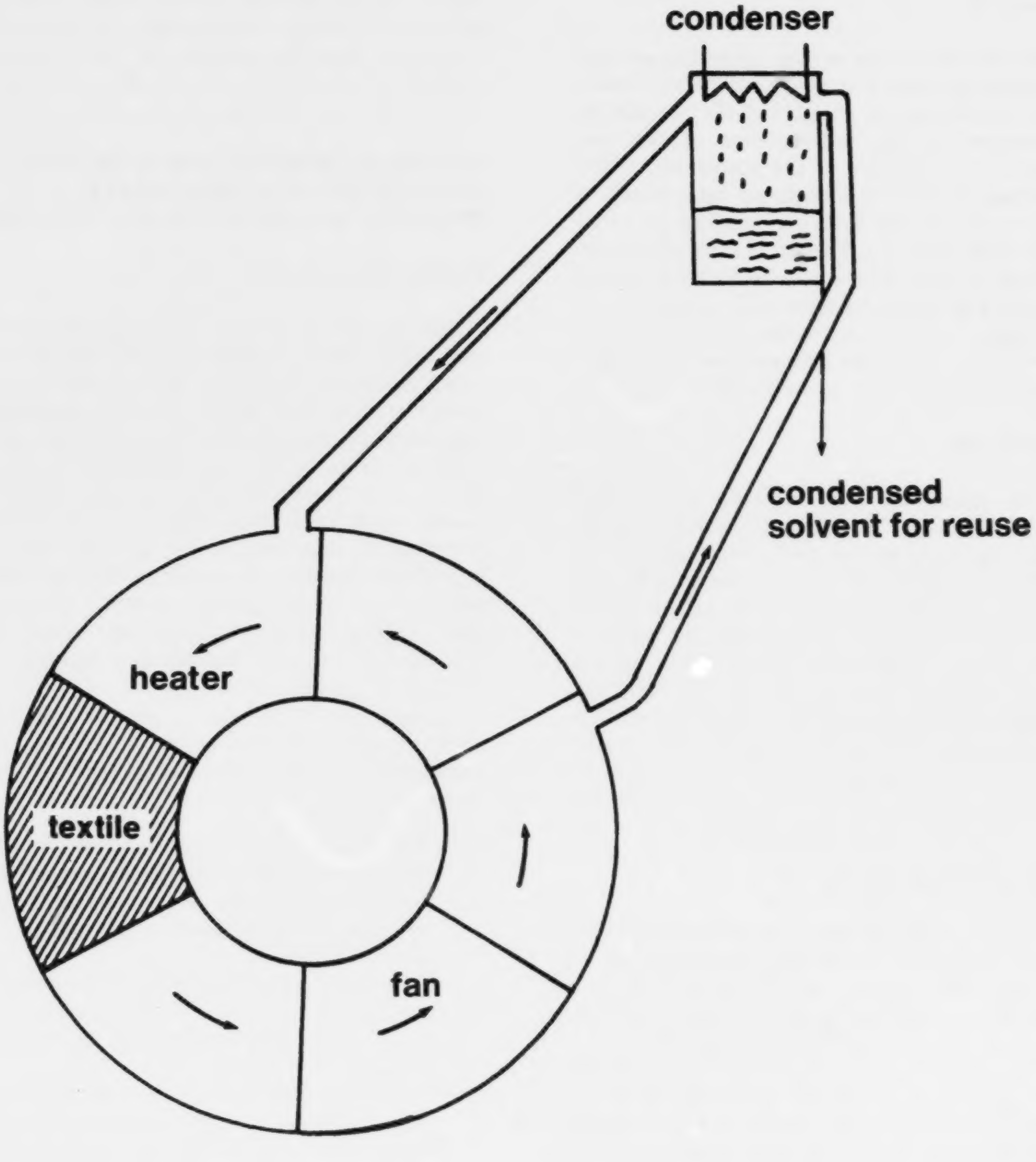

condenser
condensed solvent for reuse
heater
textile
fan

Figure 7. Principle of drying.

overall total dyeing and drying cycle is, therefore, approximately 3.5 hours.

Figure 8

At the end of the drying cycle, the air contained in the closed circuit is still mixed with a very small amount of solvent that cannot be condensed at the temperature of the condenser. The opening of the autoclave at that time would result in a slight air contamination. The figure shows that the machine is ventilated with fresh air. This air is filtered with activated carbon before release into the atmosphere. This could be done in a closed circuit, but some carbon dust would deposit back on the textile. When the activated carbon is saturated with solvent, it is reclaimed by steaming.

Sizing Oils

The sizing oils are dissolved by the perchloroethylene. The separation and the reclaiming of the perchloroethylene and the oils is done in a boiler similar to those used in commercial dry cleaning machines. At the end of the cycle, the last of the perchloroethylene is stripped by steam. In conventional dyeing cycles, the oils are lost in the effluents. The same happens with the chemical agents used in conventional dyeing. No elaboration is needed on the savings resulting from the fact that no chemical agents whatsoever are used in the STX process.

Energy Consumption

Solvent dyeing would not be feasible if solvent reclaiming required large amounts of energy. Fortunately, specific and latent heat figures are very low in the case of the solvents used, as is shown in Figure 9.

The advantages as compared to conventional water-based systems are shown in Figure 10. The energy consumptions for solvent dyeing are related to the use of a 1-metric-ton-capacity machine. These consumptions would be reduced, as well as the bath ratio, for machines having a larger capacity. Additional reductions of energy consumption would be obtained by operating under a slight vacuum, which would help in the exhaustion of methanol.

Figure 11 shows that dyeing itself, performing as it is in fiber penetration, only represents one-half of the task. The atmospheric contamination hazard, due to the use of solvents, is taken care of through closed circuit drying, with a low energy consumption (14 percent). Finally, it must be pointed out that solvent reclaiming represents a large share (32 percent) of the total energy consumption.

POTENTIAL BENEFITS AND CONCERNS ASSOCIATED WITH WIDE-SCALE IMPLEMENTATION OF THE STX PROCESS

Energy Conservation

The potential energy savings associated with STX solvent dyeing are very significant when compared with the conventional beck dyeing process. The textile industry is heavily dependent upon petroleum and natural gas (the fuels currently in shortest supply) to meet a major part of the process energy requirements. About 60 percent of the energy presently utilized is consumed in wet (water) processing, which includes the cleaning, dyeing, and finishing processes. These processes are generally energy inefficient with efficiencies of less than 20 percent typically encountered in commercial practice.

Among the important energy saving features of the STX solvent dyeing process, in comparison to the conventional wet dyeing processes, are:

- Energy consumption in the carpet dyeing industry is mainly used in the heating and boiling out of water. In the solvent dyeing process, steam utilization is reduced by over 50 percent.
- Shortages of natural gas have had a major impact on the textile industry. The solvent dyeing process does not utilize natural gas.
- The reclaiming of solvents requires only about 10 percent of the energy needed to evaporate water in the conventional system.
- The use of chemicals in the dyeing process is reduced by about 50 percent. An indirect benefit is the reduction of energy consumed in producing these chemicals.
- Carpet is dyed at lower temperatures (about 70° C) in the solvent dyeing process

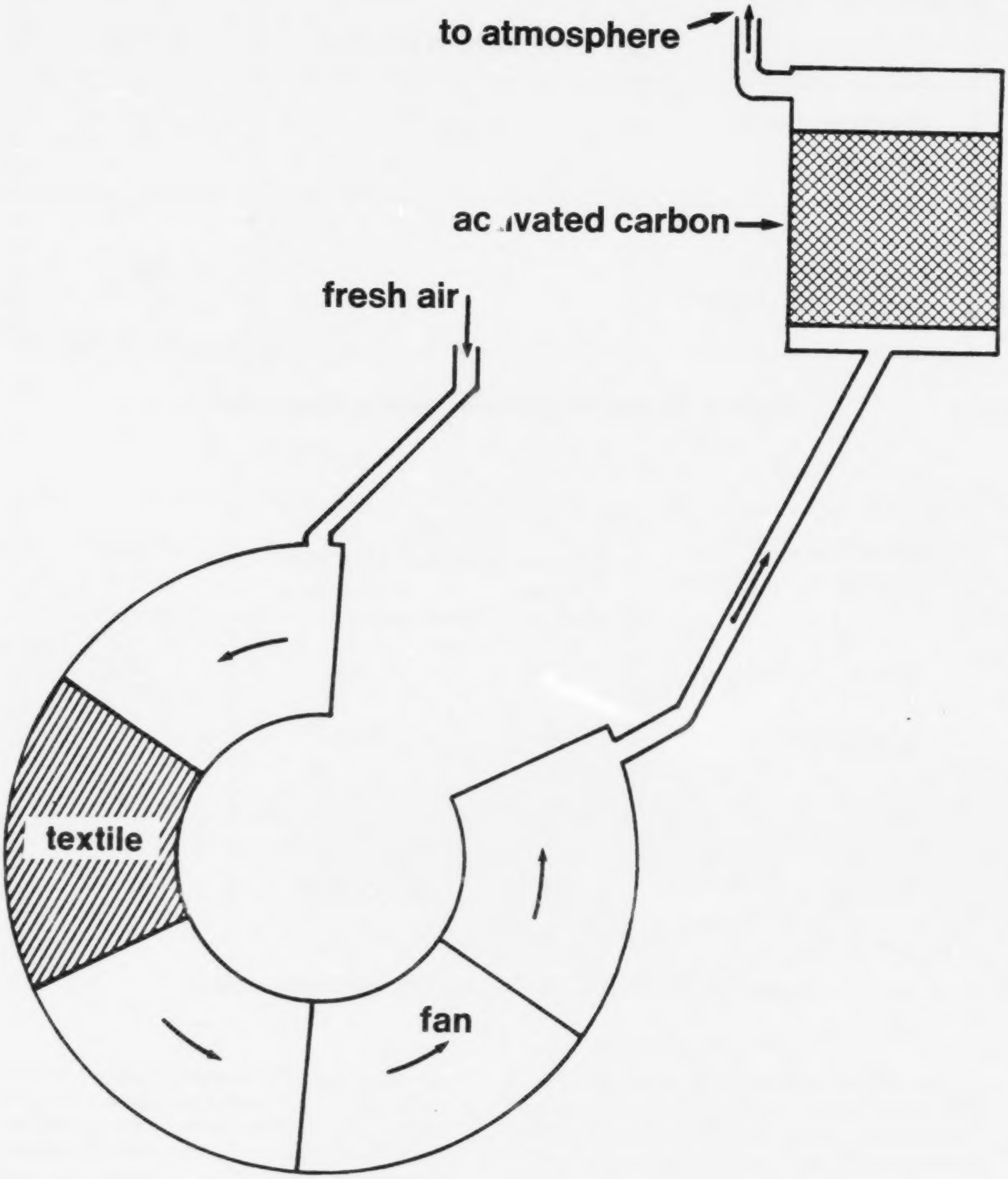

to atmosphere
activated carbon
fresh air
textile
fan

Figure 8. Principle of the ventilation.

	PERCHLORETHYLENE	WATER
SPECIFIC HEAT KCAL/KG/°C	0, 216	1
LATENT HEAT UNDER 760 MMHG	50	539

Figure 9. Specific and latent heat figures of solvents used.

ENERGY CONSUMED FOR 100 KG OF DYED CARPET	WATER WITHOUT EFFLUENT TREATMENT		SOLVENT STX
	BECKS	CONTINUOUS	
STEAM KILOGS	935	508	435
ELECTRICITY KWH	53	55	57
GAS M^3	20	20	0
TOTAL K CALORIES	803. 483 100 %	546. 248 66 %	315. 032 38 %

Figure 10. Advantages over conventional water-based systems.

The costs of treating waste discharges from the carpet industry are high. However, just as important is that the advanced treatment processes required with wet process dyeing result in the consumption of large amounts of energy.

Water Usage

The capacity of the solvent dyeing plant developed by STX is approximately 6 tons of carpet per day. To dye an equivalent amount of carpet using the beck dyeing process would require 36,000 gallons of process water since approximately 3,000 gallons of water are used with the conventional beck dye load of about 1,000 pounds.

Because of the concentration of the carpet industry in Dalton, Georgia, nearly 50 percent of

	KILOCALORIES	
BEAMING, UNBEAMING, STEAMING	10 000	3 %
DYEING	159 000	51 %
DRYING	44 000	14 %
SOLVENT RECLAIMING	102 000	32 %
	315 000	100 %

Figure 11. Breakdown of the energy consumption.

all raw water used in the carpet manufacturing process is taken from local streams in northwest Georgia. This restricts the use of these waters for other purposes because of the need to maintain flows sufficient to meet these process demands and to assimilate wastes discharged after completion of the carpet dyeing processes.

Occupational Safety

The STX solvent dyeing process uses two solvents: perchloroethylene and methanol. The process used is self-contained and both perchloroethylene and methanol are completely recycled and reclaimed.

The Occupational Safety and Health Administration (OSHA) has established an industrial standard for exposure to perchloroethylene of 100 ppm for an extended time period. In the plant built in Europe to test the solvent dyeing system, probes located in the dye house never showed a concentration above 30 to 40 ppm of perchloroethylene in the atmosphere, and this level was reached only during the limited time that the autoclave was opened at the end of each dyeing cycle.

The fact that the temperature utilized in the solvent dyeing process is quite low and never exceeds 70°C is another safety feature of the STX system since it eliminates the need for high temperature operations.

The solvent dyeing process never includes the mixing of air and methanol. In the process, perchloroethylene eliminates the air before methanol is introduced. This is strictly monitored and controlled.

The solvent dyeing plant in Europe was operated for a period of 1 year. Documentation is available that demonstrates that this plant has met all applicable U.S. safety standards during this period of operation.

Chemical Usage

The chemical usage in the STX process is limited to the dyestuffs and the small quantities of solvents lost in the process. This chemical usage level compares very favorably with the existing aqueous systems now in use, which demand that a variety of chemicals be used as dyeing assistants in order to achieve good product characteristics. The elimination of the need for these other chemicals can cut the cost of dyeing chemicals by as much as 50 percent.

Benefits to the Carpet Industry

The STX solvent dyeing system offers many potential benefits to the carpet industry as well as to other segments of the textile industry. The most apparent benefits are:

- Since water is used only for cooling and steam generation, the STX process eliminates all problems related to supply of raw water and discharge of polluted wastewater. Since carpet dyeing plants are having to cope more and more with the twofold problems of supply and pollution of water, there is a great incentive to investigate any alternative process that would solve this situation.
- The overall cost of dyeing carpet is reduced by the STX process since chemical usage, water usage, and energy usage are all reduced. There is also a cost savings inherent in the process as the process eliminates the 4 to 5 percent waste of carpet fiber that is experienced in using aqueous dyeing. These savings could potentially yield an overall dyeing cost reduction exceeding 30 percent in the carpet industry as compared to current aqueous dyeing methods.
- The subtle components of product quality in the carpet industry such as softness, luster, color fastness, and texture are either matched or improved by the STX solvent dyeing process. In a highly competitive market, such as the high quality residential carpet market, these characteristics can often be an overriding factor in the buying decision of the consumer.
- A very important benefit to carpet manufacturers offered by the STX process is the potential for more accurate color matching from one dye lot to another. If sufficiently accurate controls can be developed, the STX process will enable a manufacturer to match one dye lot to another close enough to permit installation of two different dye lots side by side without any noticeable difference in color. In conventional beck dyeing, this is not now possible even with the sophisticated measuring equipment available. The capability for color matching would offer many advantages, both in marketing and manufacturing.
- Production efficiency should be improved with the STX solvent dyeing system since dyeing cycle time is significantly reduced.
- The dyestuffs and other chemicals used in the STX process are commonly used in the carpet and textile industry, and, therefore, availability of these materials should not pose any problems.

Patent Rights

Patent rights are held for all aspects of the solvent dyeing process. Patents are held on the dyeing system employed including its chemical aspects and also on the equipment utilized. Patents are also held on the use of this system with different types of materials (nylon, wool, etc.).

in comparison to the wet dyeing process, which requires temperatures of about 100° C. This results in significant energy savings.

- Elimination of the need for the processing of raw water and the treating of process wastewater results in significant cost savings.

It is estimated that the solvent dyeing process would permit the savings of approximately 1 pound of fuel oil for every pound of carpet dyed.

Water Pollution Control

It has been estimated that the discharges from a dyeing process with a capacity of 6 tons of carpet per day (the capacity of the plant utilized in the solvent dyeing process) equal the domestic wastes of 10,000 to 15,000 people. This is indicative of the strength of the waste discharges of the carpet industry, which include high quantities of both organic and inorganic chemicals (dyes, pH control agents, lubricants, etc.). These wastes require extensive treatments prior to discharge to the natural stream system. When the strengths of these wastes are considered in the context of the large volume of waste discharged (over 100 billion gallons of water per year), the potential impact of these discharges on the water quality of receiving streams, and the costs of treating the wastes prior to discharge, become very significant.

The solvent dyeing process does not use process water. Additionally, the solvents utilized in the process are reclaimed, not discharged. Consequently, effluent problems and water quality problems associated with carpet dyeing (and potentially with all textile dyeing) could be virtually eliminated through wide-scale use of solvent dyeing.

Nylon fiber is used in nearly 90 percent of the carpet now manufactured in the United States. Since the solvent dyeing of nylon is technically proven, the potential for immediate water quality benefits could be significant in the carpet industry.

RECONSTITUTION AND REUSE OF DYEBATHS

Wayne C. Tincher,* Fred L. Cook,* L. Howard Olson,* W. W. Carr†

Abstract

A system for dyeing textiles has been developed that permits reuse of dyebaths for up to 15 times before the bath is discharged. At the conclusion of the dyeing cycle the bath is analyzed and reconstituted to the dye and chemical concentrations required for the next dyeing. The system has been used on a pilot scale for dyeing nylon and polyester carpet, nylon hosiery, and polyester yarn packages. A plant demonstration of the reuse technology for hosiery dyeing has been completed. Significant reductions in dye (19 percent), chemical (35 percent), water (43 percent), and energy (57 percent) requirements were achieved with the reuse system. The cost of materials and energy for hosiery dyeing was reduced 37 percent by reuse of the dyebath.

INTRODUCTION

The textile industry uses approximately 500×10^9 liters (125 billion gallons of water annually (ref. 1). Much of this water is discharged with appreciable quantities of organic and inorganic chemicals (dyes, pH control agents, lubricants, surfactants, auxiliaries) that require extensive treatment of the wastewater and contribute to the pollution problems associated with textile processing. In the past, the pollution problem resulting from textile processing has been attacked by construction of waste treatment facilities. As requirements became more stringent, the waste treatment plant was expanded or additional treatment processes were added to meet the standards. This approach has consumed large sums of nonincome-producing capital and has increased the operating costs of many textile plants.

In addition to problems associated with water supply and pollution control, the increasing cost and decreasing supply of energy represent a major problem for the textile industry. Energy requirements for the U.S. textile industry in 1971 (most recent comprehensive data) were equal to approximately 67 million barrels of oil (ref. 2). Industry is heavily dependent on petroleum products and natural gas (the fuel currently in shortest supply) for a major part of process energy requirements. If the industry is to adapt to the shortages or curtailments of energy, new processes or process modifications must be implemented on a broad, industry-wide scale.

Two basic types of procedures are used for textile coloration—pad-fix (continuous) processes and exhaust (batch) processes. Continuous dyeing is used primarily for long runs of a given fabric style. Because of their continuous nature and the use of relatively small volumes of dye liquor, these processes tend to be more efficient than batch processes. Exhaust processes are generally very inefficient in their use of chemicals, water, and energy and generate large volumes of waste that must be treated. Despite these disadvantages, the versatility, ease of control, and short run capability of exhaust processes make them very attractive for coloration of many textile products.

A number of different types of batch dyeing processes (beck dyeing, jet dyeing, jig dyeing, package dyeing, beam dyeing) are used in the textile industry. Batch processes were used for dyeing an estimated 5 billion pounds of textile fibers and fabrics in 1973 (ref. 3). Batch processes readily lend themselves to process modifications that can reduce energy and materials requirements for dyeing. Such modifications were a major objective of this research project.

DEVELOPMENT OF THE REUSE SYSTEM

In the conventional batch dyeing process the dyeing machine is filled with water, the goods to be dyed are entered, and the fabric moved through the bath (or the bath moved through

---

*School of Textile Engineering, Georgia Institute of Technology, Atlanta, GA.
†Engineering Experiment Station, Georgia Institute of Technology, Atlanta, GA.

Preceding page blank

the goods) to saturate the fabric with water. Chemical auxiliaries such as wetting agents, pH control agents, leveling agents, chelating agents, etc., are then added to the bath followed by the dyes. Usually the beck is heated from ambient to dyeing temperature at a rate of approximately 2°C (4°F) per minute and held at the dyeing temperature for the time required to complete the dyeing. The goods being dyed are checked for proper shade and if on-shade, the dyebath is discharged to drain. The goods are then post-scoured and/or rinsed to remove incompletely fixed dye. The goods are removed from the machine and the machine refilled with water for the next load.

If the dyebath is examined before and after the dyeing cycle, two major changes have occurred. First, most of the dye has been removed from the bath by the yarn or fabric and second, the bath is hot rather than cold. Most of the auxiliary chemicals added to the bath are still present in the same condition as they were at the start of the dyeing cycle. When the dyebath is discharged to the drain, large quantities of energy, water, and useful chemicals are lost. A more reasonable procedure would be to analyze the spent dyebath for remaining dye, to reconstitute the bath to the desired strength, and to reuse it for subsequent dyeings. Reuse of dyebaths in this way should significantly reduce the energy, water, and chemical requirements in batch dyeing.

A number of technical problems required solution before dyebath reuse could be broadly applied in batch dyeing. First, an analytical system had to be developed to simply, accurately, and economically determine the concentration of dyes remaining in the bath. The analytical technique has to be compatible with existing dyehouse personnel, space, time, and equipment constraints. Second, dyeings must be started at elevated temperatures (~75° C). The increased rate of dye adsorption from the bath at these temperatures could lead to spotting and poor levelness in the recycle dyeings. Third, materials handling procedures had to be worked out to give scouring, dyeing, and rinsing cycles compatible with current plant operating procedures. Fourth, evaluation procedures were required to insure that dyeings in recycle baths were equivalent in quality to conventionally dyed products.

Analysis System

The very strong absorption of dyes in the visible region of the spectrum provides the simplest and most precise method for determination of dye concentration. The absorbance, A, of a dye solution can be related to the concentration by the modified Lambert-Beer equation (ref. 4):

$$A = \log I_0/I = Kc$$

where I_0 is the intensity of the visible radiation falling on the sample, I is the intensity of the radiation transmitted by the sample, K is a constant including the path length of radiation through the sample and a constant related to the absorptivity of the sample at a given wavelength, and c is the concentration of the absorbing species. In mixtures of absorbing species, the absorbance at any wavelength is the sum of the absorbance of each absorbing species and is given by:

$$A_\lambda = K_1c_1 + K_2c_2 + K_3c_3 \ldots + K_nc_n.$$

This characteristic of light absorption by dyes is important in the analysis of dye mixtures of the type found in spent dyebaths. For such dye mixtures, the absorbance can be measured at a number of wavelengths and the concentration of the dyes determined by simultaneous solution of a set of linear equations of the type shown above. The wavelengths selected for the analysis are generally those for which one of the dyes gave a maximum in absorbance.

A second procedure for obtaining dye concentrations from absorbance data was developed for very complex dye mixtures. In this procedure the absorbance of the spent dyebath was measured at 16 equally spaced wavelengths from 400 to 700 nm. The dye concentrations were determined from a least-squares fit of the absorbance curve at these 16 wavelengths. A computer program in FORTRAN IV was developed to determine the concentrations of up to six dyes in a mixture by this technique.

The Lambert-Beer relationship is generally invalid for absorbing species that are not in solution. Most dye classes used in this work (acid, basic, direct, reactive) are soluble in the dyebath and the spectrophotometric analysis could be carried out directly on the dyebath. Disperse dyes, however, are not water soluble and required development of techniques to give true dye solutions. In disperse dye analysis the spent dyebath sample was placed in a separatory funnel, a measured quantity of an organic solvent (benzene or toluene) was added, and the mixture shaken to extract the dye into the organic layer. The spectrophotometric analysis was then carried out on the dissolved dye in the organic solvent. Standards for calculation of the K values for disperse dyes were treated in the same way to insure accuracy of the procedure.

Correction for absorbance of species other than dyes (background absorbance) was required also in some cases. For dyebaths containing disperse dyes and using organic solvent extraction, background absorbance presented no problem. The absorbing species other than dyes remained in the water phase. For dyes measured directly in the dyebath, a correction procedure was necessary. Samples of the textile product being dyed were treated in a "blank" bath (a bath containing all chemicals except the dyes) in exactly the same way that the yarn or fabric would be dyed. Samples of the blank dyebath were then used to obtain standard absorption data for the blank dyebath and background K values were calculated in the same way as described above for dyes. The background absorbance could then be treated like another dye. Thus, a dyebath with three dyes would be treated as if it contained four dyes with the fourth dye being the background absorbance.

A further advantage of spectrophotometers is the ready availability of a number of low cost instruments with sufficient accuracy and reproductivity for dyebath analysis. Much of the work in the current study was carried out on a single beam grating spectrophotometer costing approximately $2,000. The computations necessary in the analysis can be conveniently carried out on low-cost desk calculators or microprocessors. The calculations necessary for a four-dye mixture (or three dyes plus background) can be handled on a system costing less than $1,000. Even the least-squares fit of 16 points of the absorption spectrum can be carried out on a $3,000 minicomputer. Development of these low-cost instrument-minicomputer systems is largely responsible for consideration of dyebath reuse as a practical reality for textile dyeing.

Accurate analysis for dyebath components other than dyes has not been required. These dyebath additives generally control the dyebath environment and are not used up or removed during the dyeing cycle. In general, these components were added to the reuse baths in direct proportion to the quantity of makeup water added to baths between dyeings. For example, if 20 percent of the dyebath was lost during the dyeing (primarily due to removal with the wet goods) then 20 percent of the original quantities of pH control agents, wetting agents, etc., was added to the bath being reused. This procedure worked very well for the series of 13 and 14 dyeings in the same bath.

Evaluation Procedures

Three important characteristics of textile products dyed by the reuse procedure were measured to determine if the dyeings were of acceptable quality—the uniformity, the reproducibility, and the stability or "fastness."

The uniformity was assessed by selecting representative samples from the dyed lot and determining the color (tristimulus values) on a standard colorimeter (DIANO/LSCE Automate System). The difference in color of each specimen from the average color of all specimens was determined using the FMC II color difference formula (ref. 5). In this system one unit of color difference is defined as the minimum perceptible difference in color. Thus, spotting or unlevel dyeings could be readily identified by variations in color difference between specimens from the same dyeing.

Reproducibility of the dyeings was determined by calculation of the color differences between dyed lots and a standard dyeing of the same shade. In this calculation the color difference was determined from average tristimulus values of each dyed lot compared to a conventional dyeing, again using the FMC II equation.

In addition to instrumental measurements, samples dyed by the reuse procedure were examined visually by expert dyers to further assess the color uniformity and color reproducibility.

Dyed samples were also evaluated for resistance to color change by rubbing (crock fastness), exposure to light (light fastness), and exposure to water (wet fastness). Standard test methods recommended by the American Association of Textile Chemists and Colorists were used in the fastness evaluations.

APPLICATIONS OF THE REUSE SYSTEM

Carpet Dyeing

Initial studies of dyebath reuse were carried out on carpet samples. Preliminary bench-scale studies to evaluate the technical feasibility of dyeing in spent baths and to develop the required analytical techniques were carried out as part of a previously reported (refs. 6,7) research program. The current work was undertaken to scale-up the dyebath reuse system for carpet dyeing. All dyeings were carried out in a 1-m beck capable of dyeing 15-kg (35-lb) carpet samples. This is the same equipment normally used in a carpet dyehouse for development work. Two of the carpet experimental trials—dyeing of nylon carpet with disperse dyes and dyeing of polyester carpet with disperse dyes—are reported here.

Dyeing of Nylon Carpet With Diperse Dyes

The objective of the first trial run in the pilot-scale experiments was to dye nylon carpet to the same shade five times with reuse of the dyebath. The carpet used in these studies was tufted from Nylon 6 face yarn with a polypropylene primary backing. Both regular nylon and cationic dyeable yarns were used in the carpet, but these types of yarns were dyed to essentially the same color with disperse dyes. The carpet surface contained both cut pile and loops.

Approximately 15 kg (35 lb) of prescoured carpet were placed in the standard pilot-scale 1-m beck, cold water was added to give a liquor ratio of 25:1, approximately 375 l (100 gallons), and the auxiliary chemicals (leveling agent, 1 percent owf; complexing agent, 0.5 percent owf; pH control agent, 1 percent owf) were added. The carpet was circulated through the bath for 5 minutes and the dyes required to give a medium green shade (Disperse Blue 7, 0.03 percent owf; Disperse Yellow 3, 0.35 percent owf; Disperse Red 55, 0.04 percent owf) were added over a 15-min period. The bath was brought to the boil at 2° C/minute with direct steam injection and held at the boil for 45 minutes. The carpet was removed by hand at 95°C and rinsed three times in a separate machine. The water volume that was removed by the carpet and by evaporation (85 liters) was added to the remaining bath, and only auxiliary chemicals calculated to bring the added water to the initial concentration of auxiliary chemicals were added. The residual dye concentrations were determined using the analytical procedure detailed above. A second batch of carpet was placed in the beck after bringing the bath back to 80° C. The dyestuffs were added to the beck over a 15-min period at 80° C, the bath was brought to the boil at 2° C/minute, and the cycle continued as in the first run. The reuse sequence was repeated in three additional runs to give a total of five dyed batches.

The pilot-scale dyeings of nylon (15-kg samples) with disperse dyes were evaluated by color measurement and color difference calculations exactly as described above. Ten random samples were cut from each of the five nylon carpet sections (1m × 2m) that were dyed medium green in the reuse sequence on the 1-m beck. Color differences between the samples from the four reuse runs and samples from the initial (conventional) dyeing were calculated. The tristimulus values X, Y, and Z were obtained on the Diano instrument by measuring each sample three times against a white tile standard for a total of 30 color measurements for each carpet length. The tristimulus values were utilized with the FMC II equation to determine the end-to-end shade variation of the carpets by averaging the tristimulus values from the 30 measurements and calculating color differences in MacAdam units between the individual sample positions and the average. The average of the tristimulus values for all 30 measurements of each carpet section was calculated, and the color differences between those averages and the average tristimulus value for the conventionally dyed standard were calculated in order to determine overall lot-to-lot variation.

Color differences between each of ten individual measurements along the carpet sample and the average for the sample for each of the pilot-scale dyeings are shown in Table 1.

TABLE 1. END-TO-END COLOR DIFFERENCES IN MACADAM UNITS OF NYLON CARPET DYED WITH DISPERSE DYES

Position	Run I	Run II	Run III	Run IV	Run V
1	1.68	0.76	2.61	1.81	0.63
2	0.67	1.33	4.02	5.16	0.40
3	1.04	3.90	0.97	3.17	1.30
4	1.99	1.82	1.00	1.90	1.13
5	0.35	3.57	3.75	1.61	2.14
6	1.60	2.38	3.15	2.11	0.69
7	0.72	3.21	1.41	0.76	0.46
8	3.39	0.84	4.17	1.55	1.79
9	0.98	2.53	1.96	3.59	2.09
10	1.10	5.78	1.23	1.52	1.64

These data indicate that there is little difference in end-to-end color variation between the sample dyed in the conventional manner (Run 1) and samples dyed in recycled dyebaths (Runs II to V).

Reproducibility of dyeings in the recycled baths is shown in Table 2. The differences in color between the first run (conventional dyeing) and dyeings in the recycled baths were determined from the difference in the average color of each run and the average for Run I. It is clear from Table 2 that differences in color for samples dyed in recycled baths are well within the acceptable commercial range.

Dyeing of Polyester Carpet With Disperse Dyes

The second trial run was conducted on polyester carpet dyed with disperse dyes. In this series three shades in a color line—a light beige, a medium blue, and a rust—were selected for dyeing. These colors were actual large-volume shades currently being dyed by a leading carpet firm. The objective of this run was to dye polyester carpet seven times (3 beige, 2 blue, 2 rust) in the same dyebath utilizing the reuse technology. In addition, the run was carried out using material handling procedures that were designed to be compatible with in-plant dyeing. The following sequence was used:

1. Dye a beige carpet in conventional manner,
2. Pump dyebath to holding tank,
3. Rinse carpet 1 in beck,
4. Remove carpet 1 from beck,
5. Clean fiber from rinse water,
6. Enter carpet 2 for prescour,
7. Drop rinse-prescour water,
8. Pump dyebath to beck,
9. Dye carpet 2 beige, and
10. Repeat steps 2 through 9 for carpets 2 through 7.

TABLE 2. BETWEEN SAMPLE COLOR DIFFERENCES FOR PILOT-SCALE DYEING OF NYLON CARPET WITH DISPERSE DYES (IN MACADAM UNITS)

Run	Color difference versus control
I (control)	–
II	1.3
III	0.4
IV	0.5
V	0.5

The dyebeck was modified by the addition of a pump and insulated holding tank for this series of runs. It should also be noted that the final rinse bath was used to give the subsequent carpet a short prescour before dropping the rinse bath.

In a typical dyeing in a previously used bath, the beck was full at the beginning of the cycle with the final rinse from the previous run (at 70° C). The carpet was entered and allowed to run for 5 minutes to partially remove tufting oils and fiber identification tints. The rinse-prescour bath was then dropped and the dyebath used for dyeing the previous carpet pumped to the beck from the holding tanks. The dyebath temperature was 75° C. The bath was made up to volume with freshwater to give a 20:1 liquor ratio. The quantities of all auxiliaries (except carrier) were determined from the volume of freshwater required and added to the beck. The carpet was run for 5 minutes, the pH adjusted to between 5.0 and 5.2, and the required quantities of dyes added to the bath over a 15-min period. The carrier (10 percent owf) was then added slowly over a 15-min period. The dyebath was raised to the boil at 3° C/minute and run at the boil for 1 hour. At the end of the dyeing the bath was returned to the holding tank and analyzed for the residual dyes. The carpet was post-scoured, rinsed, removed from the beck, and air-dried.

Initial inspection of the dyed carpets suggested that good color reproducibility and uniformity had been achieved. Ten samples were cut from each of the dyed samples and the color measured on the Diano Colorimeter. Each sample was measured three times to average variations due to instrument changes and sample texture differences. Tristimulus values (X,Y,Z) were calculated from the average of the three measurements.

The base color of each dyed sample was determined by averaging the ten values obtained from the ten different samples cut from each carpet. Color uniformity was evaluated by calculation of the color difference of each of the ten samples from the average value for the carpet. These results for the seven dyed carpets are shown in Table 3. The color difference values were calculated using the FMC II color difference equation.

Color differences between the beck-dyed samples and standards prepared previously in beaker dyeings by conventional dyeing procedures have also been determined. In these calculations the average color for each carpet was determined from ten measurements, and in turn, the difference of this average from the average of ten measurements on the standard was determined. These calculations give a measure of the reproducibility of the dyeings in the recycled baths and are shown in Table 4. In addition to the usual FMC II color differences, the color differences in the new C.I.E. 1976 recommended color space, L*a*b*, are shown for comparison. With the exception of the two blue samples, the reproducibility was excellent. Reproducibility in the blue samples

TABLE 3. COLOR UNIFORMITY IN POLYESTER CARPET DYEINGS WITH DYEBATH REUSE

	Δe in FMC II units						
Sample number	Beige #1	Beige #2	Beige #3	Blue #1	Blue #2	Rust #1	Rust #2
1	1.14	1.93	1.97	1.15	2.37	1.16	1.54
2	2.97	2.58	0.97	1.00	0.93	1.51	0.81
3	3.30	0.95	0.87	1.27	0.28	1.00	2.86
4	0.99	3.40	0.99	0.64	0.89	0.76	1.23
5	0.89	1.89	1.26	0.96	1.09	1.42	2.68
6	4.28	1.44	1.70	2.46	1.29	0.53	0.47
7	0.66	0.85	1.27	2.56	0.94	2.77	0.81
8	3.03	0.93	1.73	2.02	1.23	1.39	2.03
9	4.50	1.81	1.33	0.76	1.24	0.89	1.82
10	4.49	1.64	0.74	2.33	2.82	2.92	1.44

TABLE 4. COLOR REPRODUCIBILITY IN POLYESTER CARPET DYEINGS WITH DYEBATH REUSE

Sample	FMC II Δe	CIE L*a*b* Δe
Beige #1	0.44	1.22
Beige #2	0.76	0.43
Beige #3	0.27	0.09
Blue #1	4.85	3.64
Blue #2	3.7	2.50
Rust #1	1.70	1.17
Rust #2	1.80	1.25

was at the outer limit of what can be considered acceptable commercial carpet dyeing. A comparison of the two blue samples with each other showed that they were very close together in color (△e = 1.44), but different from the standard. In both blue carpets the yellow was higher than the standard, and the samples were lighter than the standard. Addition of a small quantity of blue dye would have corrected this color difference between the samples and the standard. Since we had elected to do "no add" dyeing in this series, this dye add was not made. A slight modification of the dye formula would have corrected the small difference between the blue samples and the standard.

In addition to instrumental color measurements, the dyed carpets have been examined visually by four experienced carpet dyehouse supervisors. All four agreed that both the nylon and polyester carpet dyeings were acceptable as first-quality in both color uniformity and color reproducibility.

Measurement of the fastness properties of the dyeings to light, crocking, and water were also carried out. These results are shown in Tables 5, 6, and 7. All dyeings appeared to have commercially acceptable fastness properties.

Economic Evaluation of Carpet Dyeing With Dyebath Reuse

The energy, materials, and cost savings that are possible with reuse of the dyebath are dependent on a number of factors. These include the type of yarns, the shade being dyed, the number of times the bath is used, the type of auxiliary chemicals used, and the temperature of incoming water. All of these will influence the possible reduction in materials, energy, and cost. Calculations of these savings have been carried out based on the two pilot-scale dyeings of carpet discussed above. These savings are shown in Table 8. The reductions in dye, chemical, and water requirements with recycle of the dyebath were determined directly from the quantities of materials used in the pilot-scale dyeings. Since the beck used was

TABLE 5. EVALUATION OF LIGHT FASTNESS FOR POLYESTER CARPET DYED BY THE RECONSTITUTED DYE BATH METHOD

Color	Dyeing	24 hours	48 hours	72 hours	96 hours	120 hours
Beige	1	5	5	5	4-5	4-5
Beige	2	5	5	5	4-5	4-5
Beige	3	5	5	5	4-5	–
Blue	4	5	5	5	5	4-5
Blue	5	5	5	5	4-5	4-5
Rust	6	5	5	5	5	5
Rust	7	5	5	5	5	5

TABLE 6. EVALUATION OF FASTNESS TO DRY CROCK FOR POLYESTER CARPETS DYED BY THE RECONSTITUTED DYEBATH METHOD

Shade	Dyeing number	Rating	
		Sample 1	Sample 2
Beige	1	5	5
Beige	2	5	5
Beige	3	5	5
Blue	4	5	5
Blue	5	5	5
Rust	6	5	5
Rust	7	4-5	4-5

TABLE 7. EVALUATION OF FASTNESS TO WATER FOR POLYESTER CARPETS DYED BY THE RECONSTITUTED DYEBATH METHOD

Shade	Dyeing no.	Rating
Beige	1	5
Beige	2	5
Beige	3	5
Blue	4	5
Blue	5	5
Rust	6	5
Rust	7	4-5

TABLE 8. REDUCTION IN MATERIALS, ENERGY, AND COST BY REUSE OF DYEBATHS IN CARPET DYEING

	Reduction in percent	
	Nylon, disperse dyes 5 cycles	Polyester, disperse dyes 7 cycles
Dyes	3	7
Chemicals	65	7
Water	34	39
Energy	27	27
Cost	27	12

Cost summaries for carpet dyeing

	Nylon, disperse dyes 5 cycles		Polyester, disperse dyes 7 cycles	
	Conventional	Reuse	Conventional	Reuse
Dyes (data and cost)	2.18	2.11	10.25	9.70
Chemicals (data and cost)	1.35	0.47	7.29	6.57
Water (data and 45 cents/1,000)	0.45	0.29	0.26	0.07
Energy (calc. and $3 per 10^6 Btu)	3.99	2.91	5.43	3.74
Total cost	$7.97	5.78	22.93	20.08
Cost per pound	0.046	0.033	0.094	0.082
Savings percent	27.5		12.4	
Savings cents/pound	1.3		1.2	

not equipped with energy monitoring devices, the energy reductions were calculated. An example of the energy reduction calculations is given in Table 9.

These results suggest that significant reductions in water use, chemical requirements, energy requirements, and cost can be achieved by dyeing carpet with reconstitution and recycle of the dyebath.

The estimated cost for a medium size (10-beck) carpet mill to convert 50 percent of dyeing capacity to the dyebath reuse system is shown in Table 10. The calculation assumes the purchase of new equipment with a separate

TABLE 9. ENERGY SAVINGS FOR PILOT-SCALE DYEINGS NYLON WITH DISPERSE DYES (5 CYCLES)

Basis:
35 pounds Carpet samples, 875 pounds water (105 Gallons), 25:1 liquor ratio
Incoming water at 60° F
Makeup water required each cycle ~25 gallons
Dyeing temperature 212° F, rinse temperature 120° F
Efficiency of energy utilization at beck 90 percent
Reuse entry temperature 170° F
Steam required to hold at boil 1 pound/gal/h
Carpet retains 300 percent water between processes

Conventional dyeing

Heat bath 60° to 212° F (152° × 875 pounds × 1.11 × 1 Btu/pound) = 14.76×10^{4} Btu
Heat carpet 60° to 212 ° F (152° × 35 pounds × 1.11 × 0.5 Btu/pound) = 0.30×10^{4} Btu
Hold at boil for 45 min. (105 Gal × 1,000 Btu/lb × 0.75 h) = 7.88×10^{4} Btu
Rinse at 120° F (60° × 770 pounds × 1.11 – [140 pounds × 92° + 35 pounds × 92° × 0.5]) = 3.68×10^{4} Btu
Total per cycle = 26.62×10^{4} Btu
Total 5 cycles = 1.33×10^{6} Btu
Btu/pound carpet = 7,600

Reuse dyeing

Heat makeup water 60° to 170° F (110 × 100 pounds × 1.11 × 1 Btu) = 1.22×10^{4} Btu
Heat retained prescour water 120° to 170° F (50° × 100 pounds × 1.11 × 1 Btu) = 0.56×10^{4} Btu
Heat bath 170° to 212° F (42° × 875 pounds × 1.11 × 1 Btu/pound) = 4.08×10^{4} Btu
Heat carpet 120° to 212° F (92° × 35 pounds × 1.11 × 0.5 Btu/pound) = $.18 \times 10^{4}$ Btu
Hold at boil 45 min. (105 Gal × 1,000 Btu/gal × 0.75 h) = $7.88 \quad 10^{4}$ Btu
Rinse at 120° F (60° × 770 pounds × 1.11 – [140 pounds × 92° + 35 pounds × 92° × 0.5]) = $3.68 \quad 10^{4}$ Btu
Total per reuse cycle = 17.60×10^{4} Btu
Total cycles (1 conventional + 4 reuse) = 0.97×10^{6} Btu
Btu/pound carpet dyed = 5,543

Energy savings – 27 percent
Energy savings – 2,057 Btu/pound carpet dyed

TABLE 10. PAYBACK ON CAPITAL COSTS

Basis:
Plant with 10 becks – 5 to be modified for reuse
Capacity 2,000 pounds per cycle, 6 cycles per day per beck
No additional personnel required
Savings using dyebath reuse, 1¢ per pound of carpet dyed
No productivity increases are assumed

Capital costs:	Hold tanks (new)	20,000 each × 5	100,000
	Pumps	3,000 each × 5	15,000
	Piping, valves	1,500 each × 5	7,500
	Analysis equipment		7,000
		Total cost	129,500

Returns:
Production 5 becks × 2,000 pounds/beck × 6 cycles/day = 60,000 pounds/day
Returns per day 60,000 pounds/day × 1¢ /pound = $600/day

Payout: $129,500/$600 = 216 days

holding tank and pumping system for each of the five becks. At an estimated savings of 1 cent per pound of carpet dyed (considerably less than indicated in the previous cost analysis) the payback time for the installation is less than 1 year.

Batch Dyeing of Nylon Pantyhose

Hosiery is colored exclusively by batch dyeing processes. The two main types of equipment utilized are the overhead paddle machine and the rotating drum machine. In hosiery dyeing a very limited range of dyes and auxiliaries is employed. Thus, hosiery dyeing presented an excellent opportunity for application of the reuse dyeing technology.

Nylon pantyhose dyeing was selected for initial pilot-scale studies. Both Nylon 6 and Nylon 66 are used in pantyhose and both types are dyed to various shades of brown and black with disperse dyes. The same three disperse dyes are used to produce the majority of shades.

An 8-lb rotary drum machine was equipped with a holding tank and pumping system for the reuse studies. Recipes for three Nylon 66 shades (light, medium, and dark brown) and two Nylon 6 shades (medium and dark brown) were obtained from a leading hosiery manufacturer. Preliminary experiments indicated that these shades could be dyed in any desired order by reconstitution and reuse of the dyebath. The dyeing procedure developed for the experimental trial is shown in Table 11. The first cycle is a conventional dye cycle with each reuse cycle after the first essentially identical. Note that in the reuse runs the rinse water from the previous cycle was used for a quick prescour of the hosiery before dyeing. This prescour was used to partially remove knitting

TABLE 11. PROCEDURE FOR DYEING PANTYHOSE WITH DYEBATH REUSE

I. Dyeing batch I – Conventional cycle
  1. Load machine
  2. Fill with cold water, raise to 90° F
  3. Add auxiliary chemicals (1 percent dyeing assistant, 1 percent leveling agent, 0.5 percent wetting agent) run 10 minutes
  4. Add dyes
  5. Raise temperature 3° F/minute to 170° F
  6. Run 20 minutes at 170° F
  7. Sample, make adds if necessary
  8. Pump dyebath to holding tank, sample and analyze
  9. Refill with cold water
  10. Heat rapidly to 110° F
  11. Add softener and run 10 minutes at 110° F
  12. Unload machine

II. Dyeing batch II – Reuse cycle
  1. Load machine
  2. Add prescour chemical (1 percent dyeing assistant) to finish bath in machine
  3. Run 5 minutes
  4. Discharge finish-prescour bath to drain
  5. Pump dyebath from holding tank to dyeing machine
  6. Add necessary auxiliaries to reconstitute the bath
  7. Add dyes to reconstitute the bath slowly from add tank (~10 minutes)
  8. Raise temperature 3° F/minute to 170° F
  9. Run 20 minutes at 170° F
  10. Sample, make adds if necessary
  11. Pump dyebath to holding tank, sample and analyze
  12. Finish as above (Steps 9-12)

III. Dyeing batches III, IV, V, etc. – Same as batch II oils and fiber finish that could build up in the dyebath and affect the reuse dyeing.

The fibers and shade dyed in the pilot-scale run are shown in Table 12. Approximately 8 pounds of pantyhose were dyed in each run. All shades were dyed with the same red, yellow, and blue disperse dyes. It should be noted that both fiber types and light and dark shades were randomly mixed during the 13 runs.

Five specimens were cut from the legs of each of three pairs of pantyhose randomly chosen from each of the 13 runs and the colors of each specimen measured on the Diano LSCE Automate. Color differences were calculated between the samples from each run and plant standards for each of the shades. These color differences (calculated by the FMC II equation) are shown in Table 12. Similar measurements on color tolerance standards used by the plant for two of the shades gave a color difference of 7.8 for the Medium II shade and 2.9 for the Dark II shade. Thus, color differences for the reuse dyeings were well within commercial standards for those shades. In fact, all dyeings were well within normally accepted standards for hosiery dyeing. The dyed hosiery were returned to the participating company and were shipped as first-quality goods.

PLANT DEMONSTRATION OF DYEBATH REUSE TECHNOLOGY

Based on the successful pilot-scale work on dyeing with reconstitution and reuse of dyebaths, a plant-scale demonstration of the reuse technology has been conducted. The demonstration was carried out in the dyehouse of the Ladies' Wear Division of the Adams-Millis Hosiery Company.

A standard 45-kg (100-lb) rotary drum machine was modified by addition of a holding tank, pumping system, water meter, and steam measuring equipment. The machine had been equipped previously with a temperature control system and an add tank. Thus, the dyeing machine could be operated in both the conventional manner and in the dyebath reuse mode with monitoring of all materials and energy inputs. In addition to machine modification, the dyehouse laboratory purchased a Bausch and Lomb Spectronic 100 spectrophotometer and a Hewlett-Packard Model Number 9815A computer for use in dyebath analysis. Cost of the analytical equipment and computer was approximately $7,000. An interface was constructed so that the computer could read absorbance data directly from the spectropho-

TABLE 12. DYEING OF NYLON PANTYHOSE WITH DYEBATH REUSE

Run number	Fiber type	Shade*	Color difference versus standard
1	66	Light I	2.0
2	66	Medium I	4.2
3	6	Medium II	2.9
4	6	Dark II	1.9
5	66	Dark I	2.8
6	66	Light I	2.0
7	66	Medium I	3.0
8	6	Medium II	2.2
9	6	Dark II	2.4
10	66	Dark I	2.4
11	66	Light I	3.0
12	6	Medium II	3.4
13	66	Light I	4.2

*A total of 5 shades were utilized. The numeral I refers to a Nylon 66 shade, and the numeral II refers to a Nylon 6 shade.

tometer. Programs were written to permit the computer to calculate and print out the quantities of dyes and auxiliary chemicals needed to reconstitute the spent dyebath to the level desired for the subsequent dyeing.

Before beginning the reuse study, 15 conventional dye cycles were run to provide baseline data for comparison with the reuse dyeings. Energy, water, dye, and chemical requirements for pantyhose dyeings were determined from this 15-cycle run.

Following the 15 conventional dye cycles, 3 series of dyeings were carried out with reconstitution and reuse of the dyebath. In the first series the dyebath was used five times before discharge to drain. This series served to check out the reuse system and establish operating procedures. The second series consisted of 17 dyeings in the same dyebath. In this series the rinse water from each cycle was used to prescour the next load to be dyed similar to the laboratory dyeings. The third series, consisting of 14 dyeings in the same bath, was conducted in the same manner as Series II except that the hosiery was not scoured before dyeing. Materials and energy requirements for the reuse dyeings were monitored in exactly the same way as the conventional dyeings.

The sequence of dyeings in the Series II, 17-cycle run, is shown in Table 13. It should be noted that both fiber types and light and dark shades were indiscriminately mixed in the run.

TABLE 13. SERIES II SEVENTEEN REUSE CYCLES

21	Nylon 66	Light shade
22R	Nylon 66	Medium shade
23R	Nylon 6	Medium shade
24R	Nylon 6	Dark shade
25R	Nylon 66	Dark shade
26R	Nylon 66	Light shade
27R	Nylon 6	Medium shade
28R	Nylon 66	Light shade
29R	Nylon 6	Medium shade
30R	Nylon 6	Dark shade
31R	Nylon 66	Light shade
32R	Nylon 66	Medium shade
33R	Nylon 6	Medium shade
34R	Nylon 6	Dark shade
35R	Nylon 66	Medium shade
36R	Nylon 66	Light shade
37R	Nylon 66	Medium shade

No problems were encountered in dyeing a light shade following a dark shade.

The materials and energy requirements for the 15-cycle conventional dye series and for the 17- and 14-cycle reuse series combined are shown in Table 14. It is apparent that the reuse dyeings gave substantial reduction in energy, water, chemical, and dye requirements. The dye savings are related, of course, to the particular shades dyed in the various runs but reduction in chemicals, water, and energy are essentially independent of the shades being dyed. Cost reductions achievable with reuse dyeing are shown in Table 15. Dyeing costs were calculated using current quoted prices for chemicals, dyes, energy, water, and sewer service.

Several important aspects of plant implementation of dyebath reuse were revealed by the demonstration runs. First, the analysis time was reduced during the course of the demonstration from 30 minutes to approximately 10 to 15 minutes with no apparent loss in required accuracy. In this time the analysis could be readily completed during the usual rinse cycle and the dyes weighed and readied for the next load.

Second, the third series of dyeings indicated that prescouring of the hosiery was unnecessary. No differences in the analysis of the bath or the quality of the dyeings were detected in the third series. Removal of the prescour step provided a dyeing cycle more compatible with the normal plant operation. About the only difference in Series III runs and conventional runs was that at the conclusion of dyeing; the dyebath was pumped to a holding tank rather than being discharged to the drain and the beck was filled with used dyebath rather than freshwater in the subsequent cycle.

Careful records were kept of the number of adds required to produce the desired shade in both conventional and reuse dyeings. Savings from dyebath reuse could be rapidly lost if more adds were necessary in reuse dyeings. The 15 conventional cycles required a total of 11 adds for an add rate of 0.73 adds per cycle. The 31 reuse cycles required 12 adds for a rate of 0.39 adds per cycle. Thus, the number of adds required in the reuse dyeings was actually 47 percent less.

The hosiery dyeing plant runs clearly demonstrated that reuse dyeing can be incor-

TABLE 14. MATERIALS AND ENERGY REDUCTION REUSE DYEING

Energy		
	Conventional	2.18 pounds steam/pound fiber dyed
	Reuse	0.94 pounds steam/pound fiber dyed
	Reduction	57 percent
Water		
	Conventional	4.08 gallons/pound fiber dyed
	Reuse	2.31 gallons/pound fiber dyed
	Reduction	43 percent
Chemicals		
	Conventional	1.17 ounces/pound fiber dyed
	Reuse	0.76 ounces/pound fiber dyed
	Reduction	35 percent
Dyes		
	Conventional	0.0058 pounds/pound fiber dyed
	Reuse	0.0047 pounds/pound fiber dyed
	Reduction	19 percent

TABLE 15. ENERGY AND MATERIAL COST REDUCTION IN REUSE DYEINGS

Cost per dye cycle:		
	Conventional	$4.66
	Reuse	$2.98
Cost per pound of fiber dyed:		
	Conventional	5.25 ¢
	Reuse	3.28 ¢
Cost reduction:		37 percent

porated in a commercial operation with no loss in quality or productivity and with substantial savings in materials and energy costs. Additional plant demonstrations of the reuse technology are planned for carpet dyeing and for dyeing of polyester/cotton blend yarn packages. Laboratory work is also being carried out on jet dyeing of knit fabrics.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the funding of this work by the U.S. Department of Energy. Further details on reuse technology will appear in reports issued by that department.

The plant demonstration phase of this work was made possible by the generous support and assistance of the management and personnel of the Adams-Millis Hosiery Company.

The substantial contributions to the laboratory phase of the project by Mrs. Lynn Averette and Mr. Jimmy Wadia, student research assistants, are gratefully acknowledged.

REFERENCES

1. U.S. Environmental Protection Agency, "In-Plant Control of Pollution: Upgrading Textile Operations to Reduce Pollution," Environmental Protection Agency Technology Transfer Seminar Publication, EPA-62513-74-004, October 1974.
2. J. F. Lowry, et al., "Energy Conservation in the Textile Industry," Phase I Technical Report, Department of Energy Project, E(40-1)-5099, Engineering Experiment Station, Georgia Institute of Technology, Atlanta, GA, p. 36, April 1977.
3. J. F. Lowry, "Energy Conservation in the Textile Industry," Phase I Technical Report, Department of Energy Project, E(40-1)-5099, Engineering Experiment Station, Georgia Institute of Technology, Atlanta, GA, p. 29, April 1977.
4. C. Giles, *Notes for a Laboratory Course in Dyeing,* Society of Dyers and Colorists, Yorkshire, England, p. 53, 1966.
5. D. B. Judd and G. Wyszecki, *Color in Business, Science and Industry,* Third Edition, John Wiley and Sons, New York, p. 322, 1957.
6. W. C. Tincher, "Conservation of Water, Chemicals and Energy in Dyeing Nylon Carpet," Final Technical Report ERC-07-77, Office of Water Research and Technology Project A-064-GA, School of Textile Engineering, Georgia Institute of Technology, Atlanta, GA, November 1977.
7. W. C. Tincher, *American Dyestuff Reporter,* Vol. 66, No. 5, p. 36, 1977.